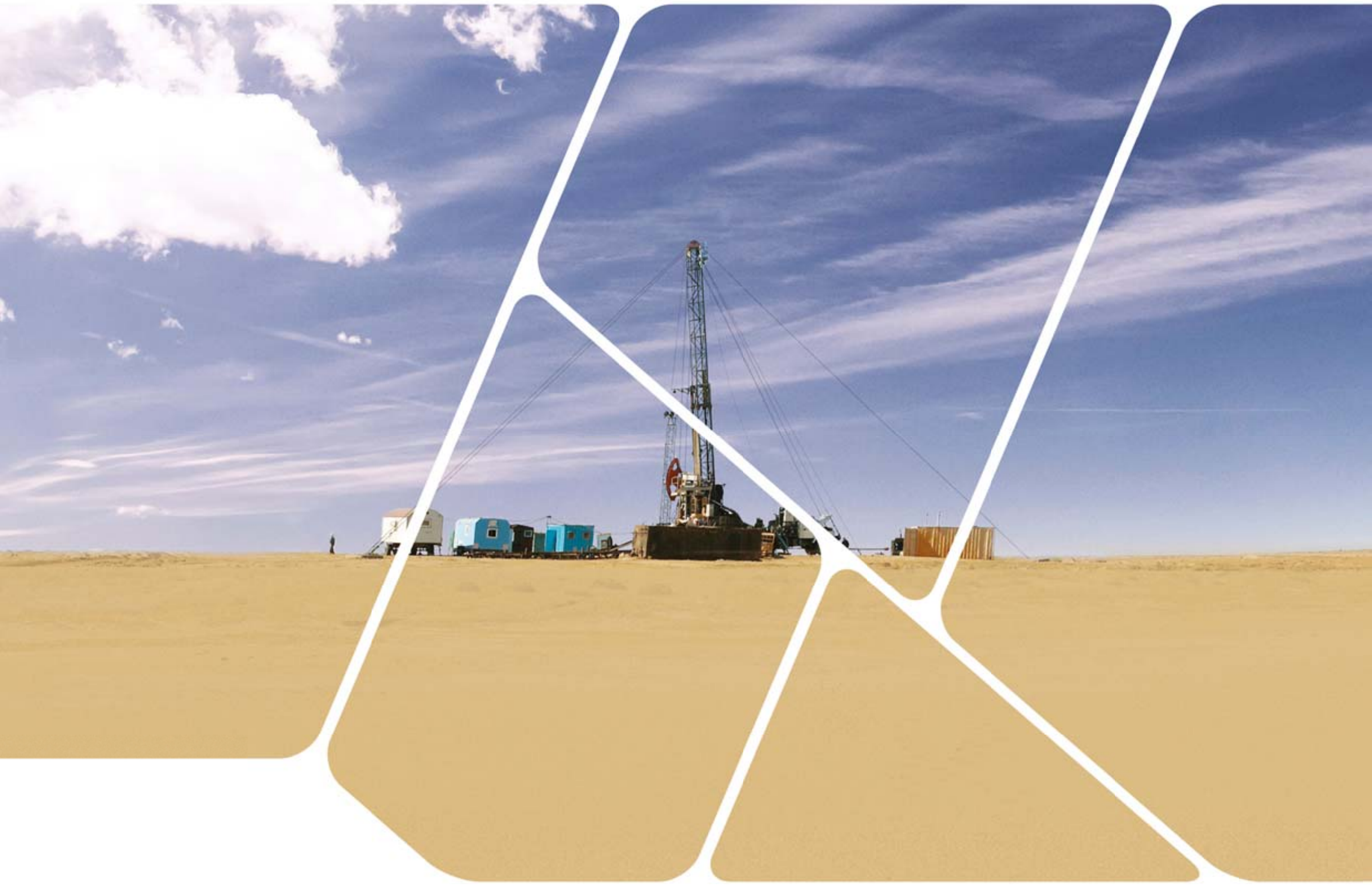


RESERVOIR ENGINEERING GRADUATE CERTIFICATE - *Week 2*

Fluid studies -PVT

A special course by IFP Training for REPSOL ALGERIA
Alger – November 06 - 10, 2016

ifptraining.com

An IFP Training Course for REPSOL

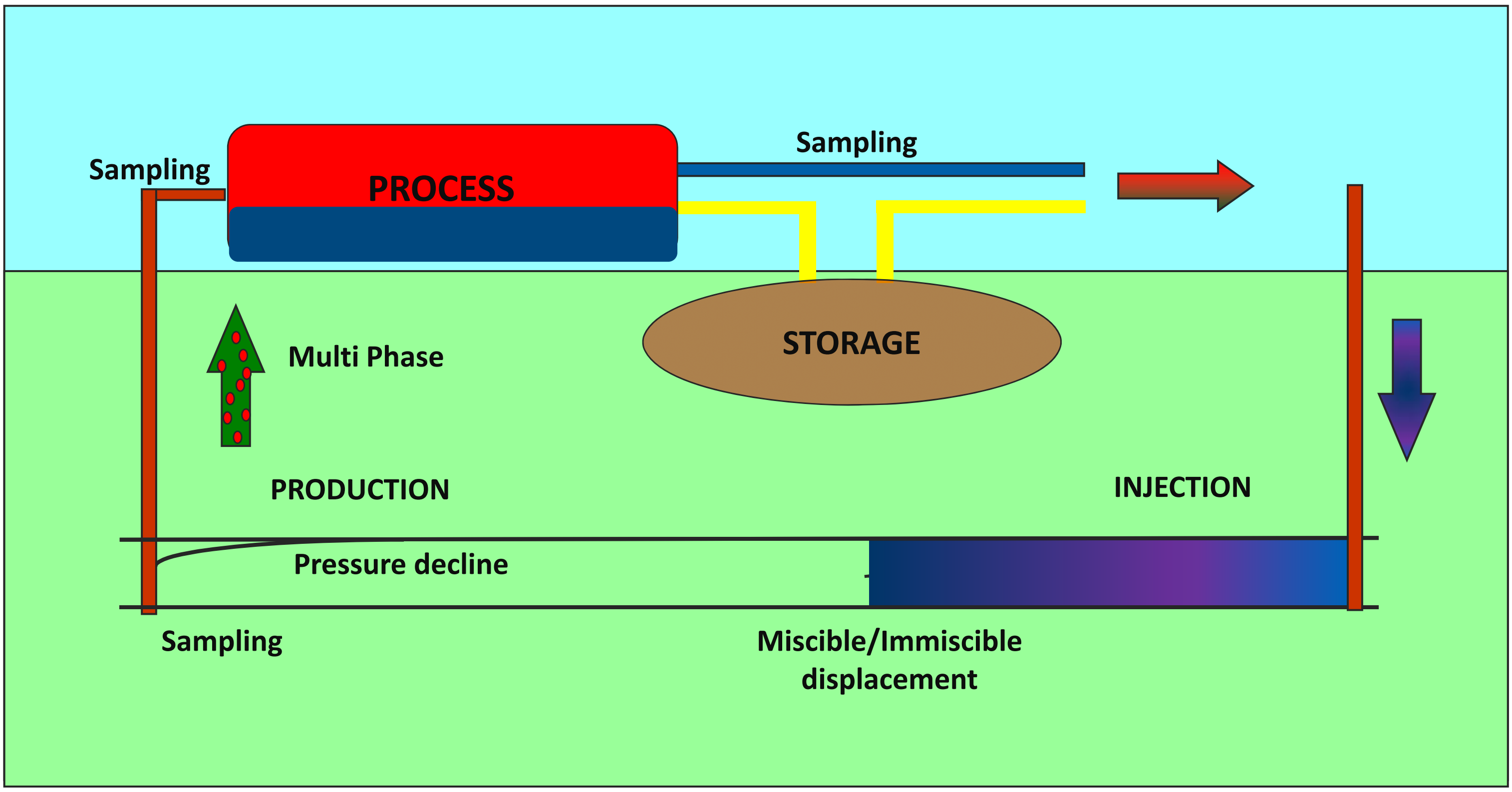
Fluid studies PVT

Instructor: Patrick ELHORGA

Fluid studies PVT – Summary

1. Preface

Preface



Preface

We need to know

1. **The composition of the production well stream and its temporal variation**
2. **The separator specifications including LPG**
3. **The design of the completions by identifying the spatial fluid distributions in the vicinity of the wellbore**
4. **Gas injection/re-injection**
   - Identifying gas composition
   - The interaction of the injected gas and the reservoir fluid

Preface

AND

5. **The ultimate recoveries of components, under different drives, mixing/no mixing, single depletion, etc.**
6. **The amounts and composition of liquids left in the reservoir not recovered (especially in gas condensate reservoirs) and their properties: density, Surface Tension, viscosity.**
7. **To detect spatial variation of the PVT properties**
8. **To identify and adjust data inconsistencies**

Preface

AND

For Reservoir Performance simulation software:

9. **To create "Black-Oil" PVT tables for Black Oil Simulation**

10. **To create Compositional PVT models for compositional simulation**

Preface

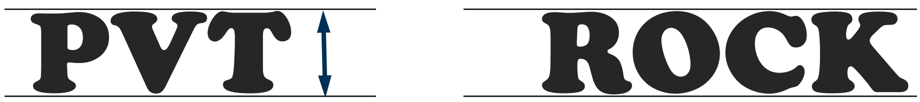
OBJECTIVE OF GATHERING AND ANALYZING PVT DATA

- **To calibrate models (Equations of State, EOS)**
- **Why?**
  - We cannot measure all the characteristics of hydrocarbon fluids. EOS provides one consistent source of PVT data
  - Experiment problems (cost, reliability, accuracy and precision)

PVT

- Sometimes people spend a lot of time on the rock characteristics and put less emphasis on fluid PVT.

- Fluid PVT is as important as rock properties as it is directly related to reserves and the dynamics of the reservoirs for performance estimations



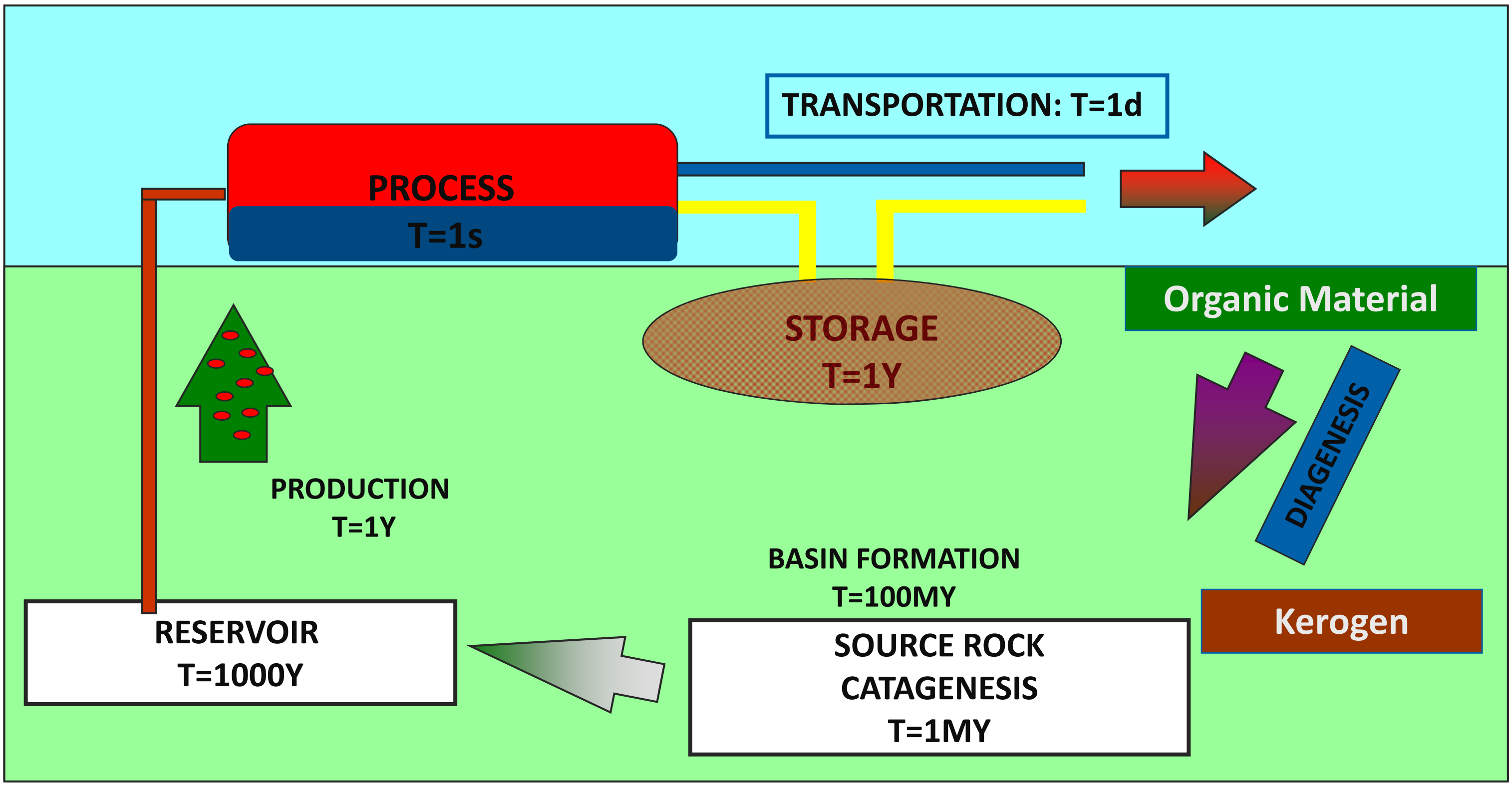
2. Reminders on thermodynamics

Summary

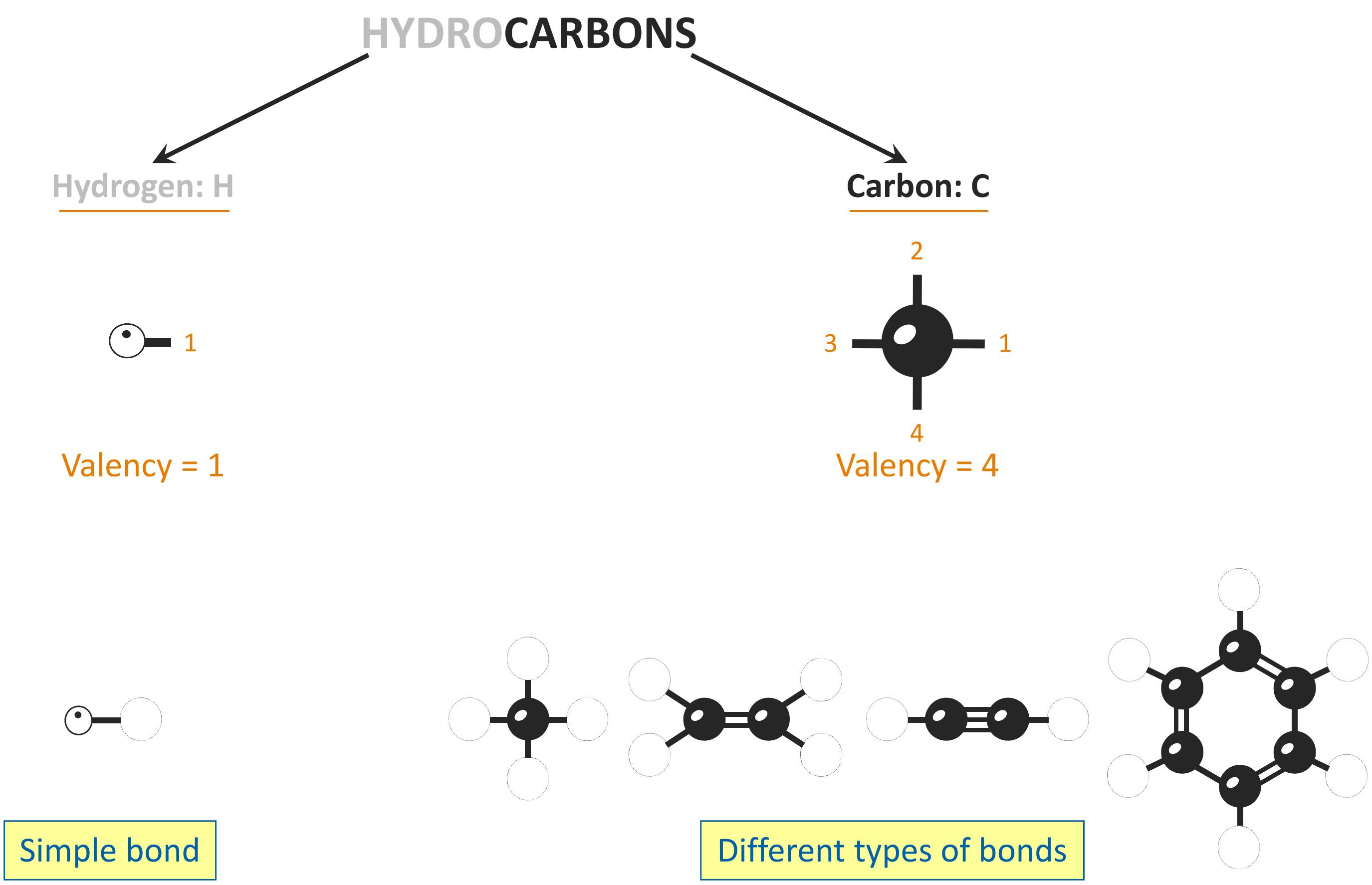
Petroleum genesis

Summary

Petroleum genesis



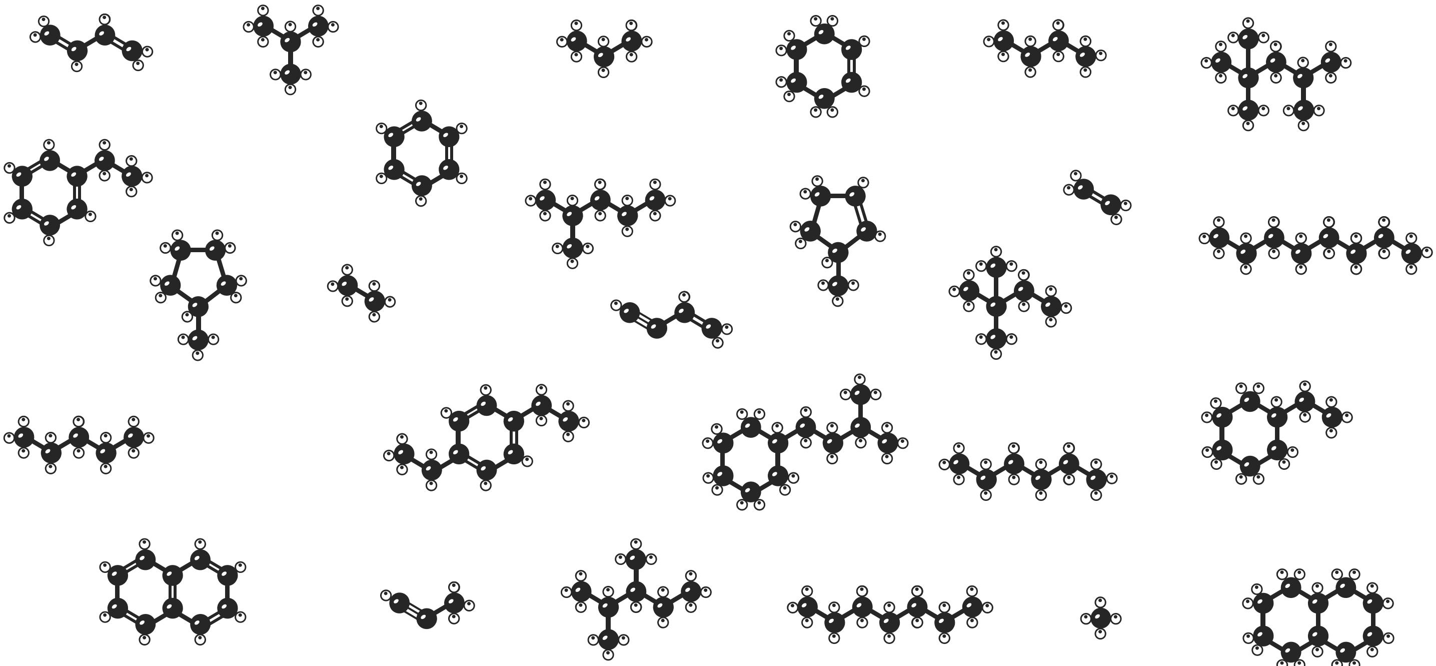
Petroleum genesis: Hydrocarbons



Petroleum genesis: Hydrocarbon classification into groups

CARBON atom of Valency 4
&
Different types of bonds

HYDROCARBONS of different size and shape.



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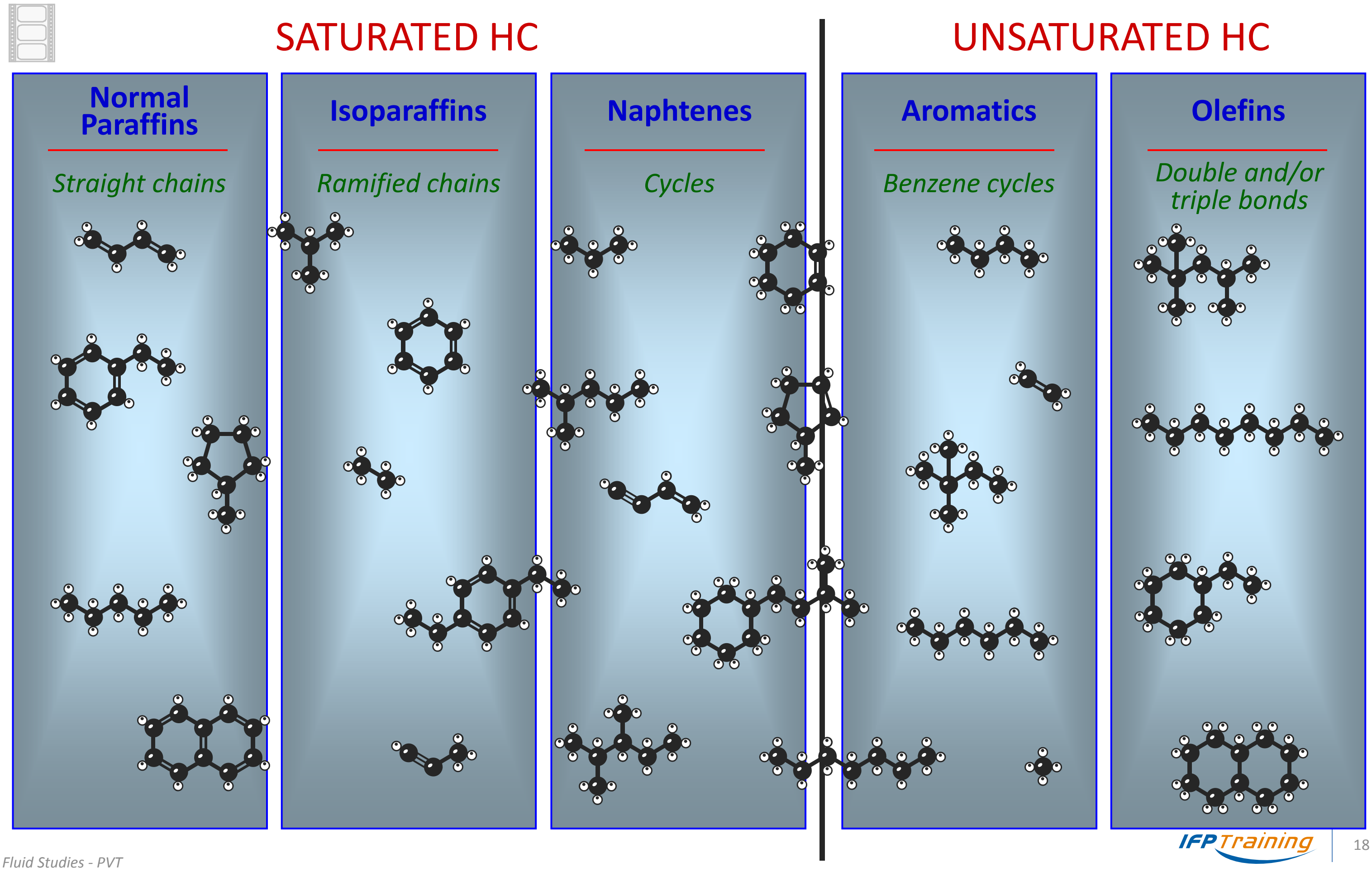
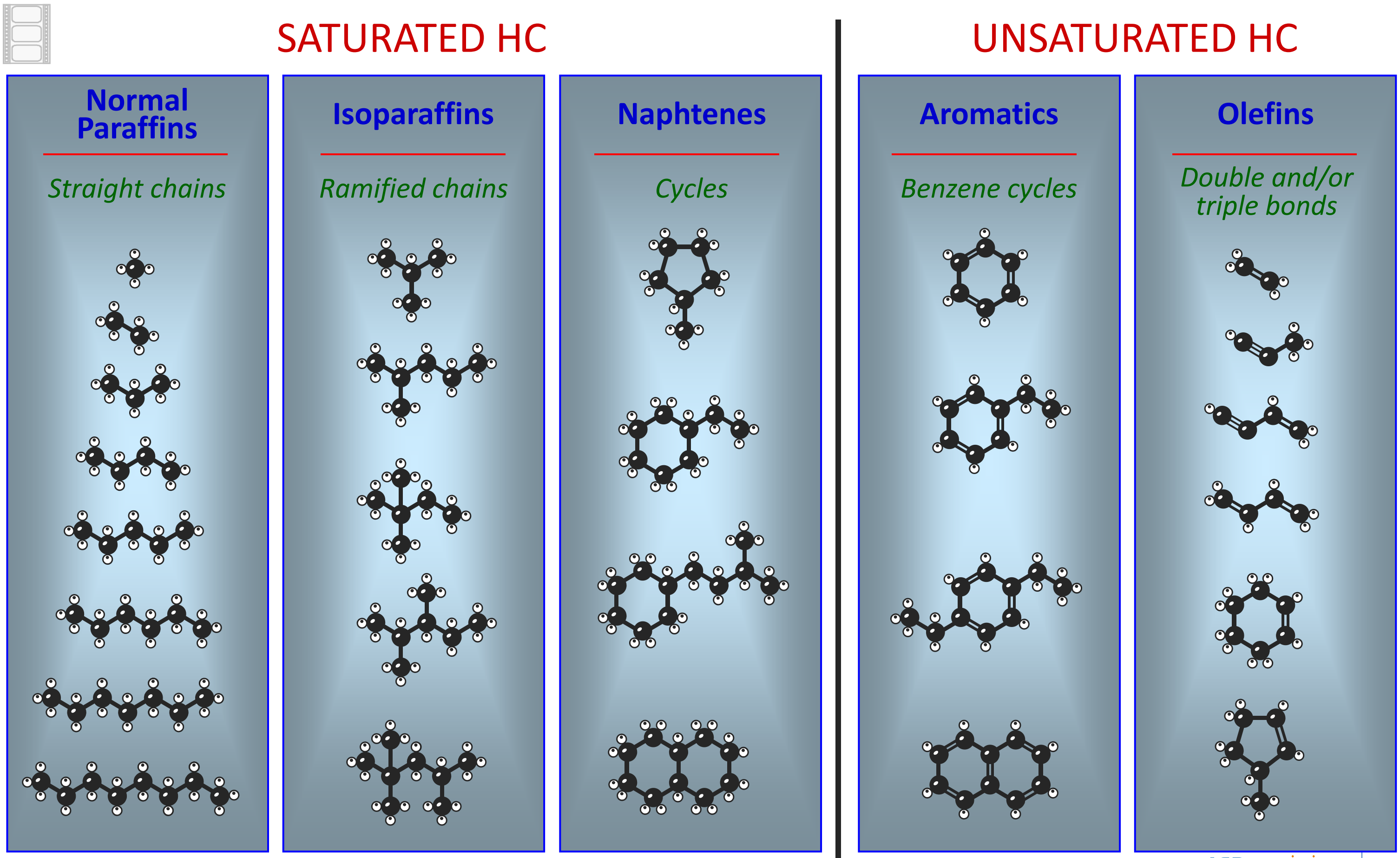


Petroleum genesis: Hydrocarbon classification into groups



Petroleum genesis

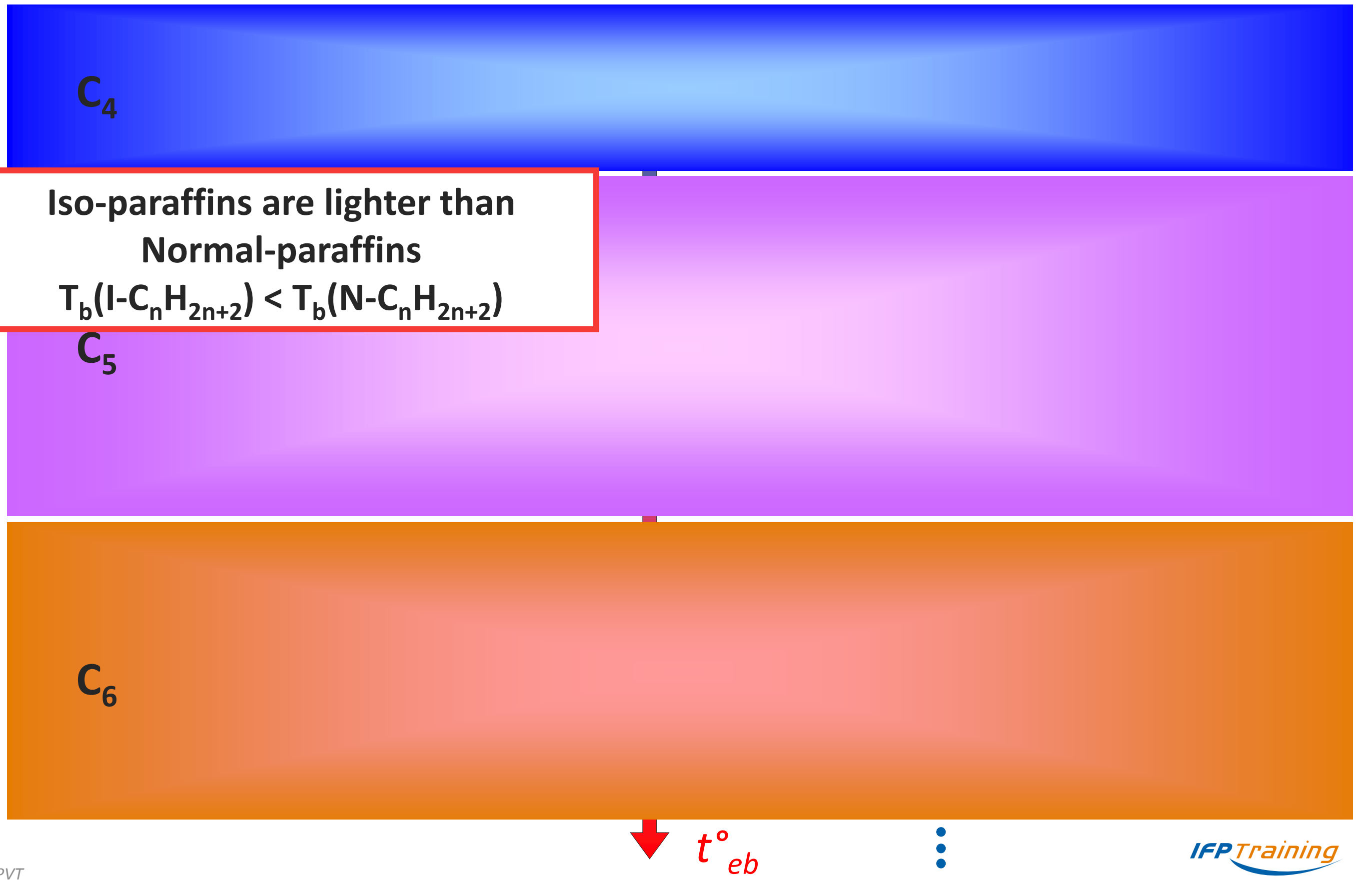
NORMAL and ISO ALKANES: $C_n H_{2n+2}$

- **Group of hydrocarbons consisting of linear molecules with the formula C_nH_{2n+2}. Methane, CH_4, is the simplest member. Higher members, starting at about C_{18}, are wax-like and are called paraffins.**

CYCLO ALKANES: $C_n H_{2n}$

- **At low carbon numbers Cycloalkanes are less stable than normal alkane counterparts**
  - thus present in much smaller amounts
  - but can have significant effect on the phase behavior

Normal boiling point of paraffins



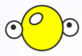
Iso-paraffins are lighter than Normal-paraffins
$T_b(I\text{-}C_nH_{2n+2}) < T_b(N\text{-}C_nH_{2n+2})$

Aromatics

- Aromatic hydrocarbons contain one or more benzene rings
- Stable rings with 3 carbon-carbon double bonds - C_6H_6
- They have some significant effect on the phase behavior.

Non Hydrocarbons: Sulfur components

Hydrogen sulfide



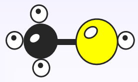
NBP = - 60°C

H_2S

Gaseous, extremely TOXIC, Corrosive

Mercaptans

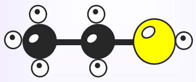
- *Methyl-mercaptan*



NBP= 6°C

CH_3SH

- *Ethyl-mercaptan*



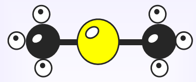
NBP = 35°C

C_2H_5SH

Acidic components, bad smell

Sulfides, Disulfides,…

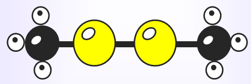
- *Di-methyl-sulfide*



NBP = 37°C

CH_3SCH_3

- *Di-methyl-disulfide*



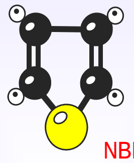
NBP = 109.6°C

$CH_3S_2CH_3$

Non acidic, BUT decompose due to heating into mercaptans

Thiophenic compounds

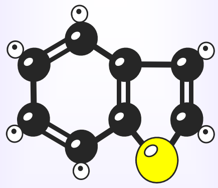
- *Thiophene*



NBP = 84°C

C_4H_4S

- *Benzo-thiophene*



NBP = 220°C

C_8H_6S

Non acidic components

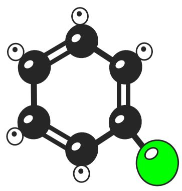
Non Hydrocarbons: Other components

Non hydrocarbons

- **Nitrogen – Pyridine – Most others are unstable**

C_6H_5N

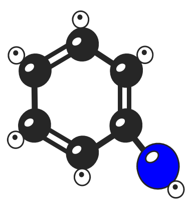
- *Pyridine*



- **Oxygen – Aromatic alcohols, aldehydes, carboxylic acids**

- *Phenol*

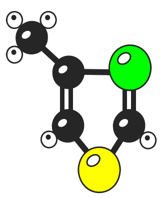
C_6H_5OH



- **Organo – Metallic – Trace amounts**

- *Methylthiazole*

C_4H_6SN



Some definitions

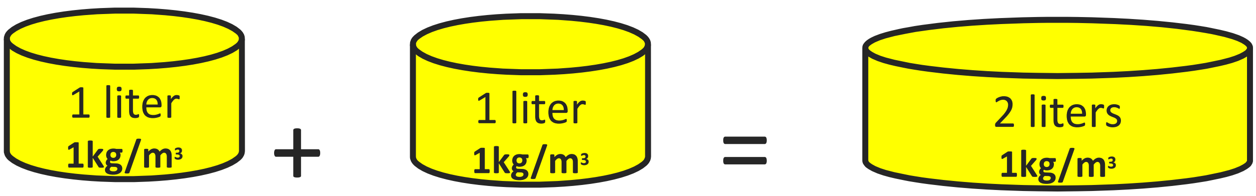
Intensive properties

- They do not depend on the quantity of material (density, viscosity, permeability)

Extensive properties

- They depend on the quantity of material (mass, volume)

Extensive properties can be summed but intensive properties require specific averaging



Some definitions

Isothermal

- An isothermal process takes place at constant temperature

Isobaric

- Isobaric processes occur under conditions of constant pressure

Isochoric

- Describes a process or system change which takes place at constant volume

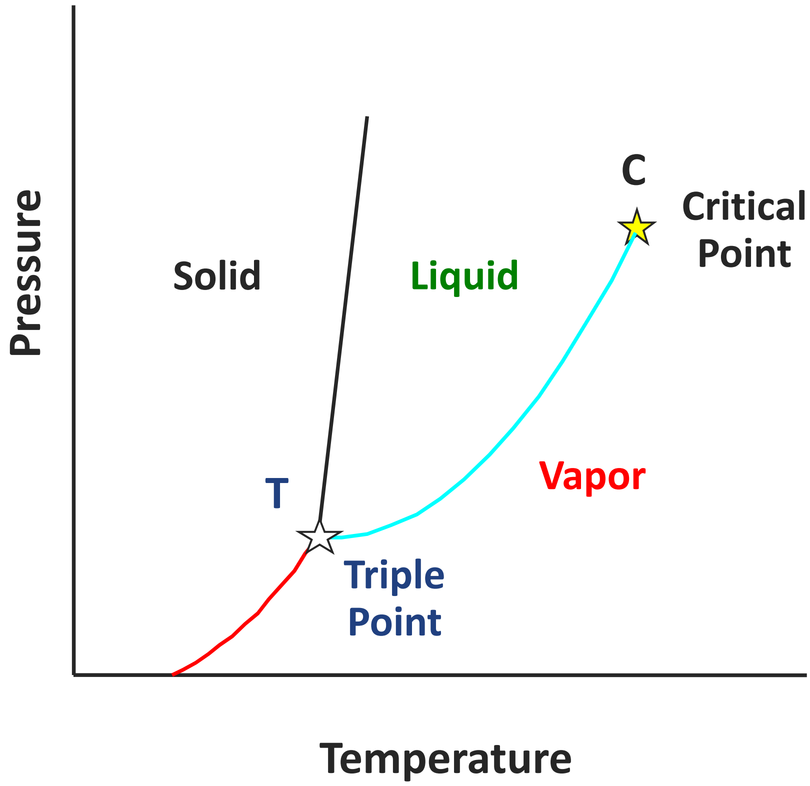
Isenthalpic

- Describes a process or system change which takes place at constant enthalpy

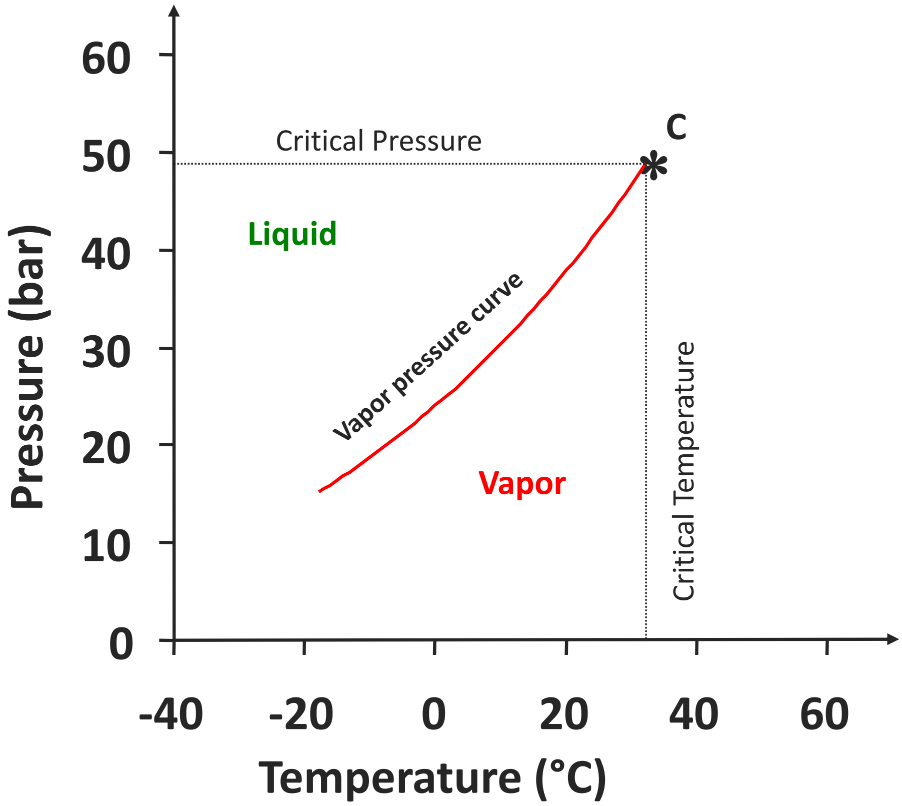
Pure component and mixture equilibrium

Summary

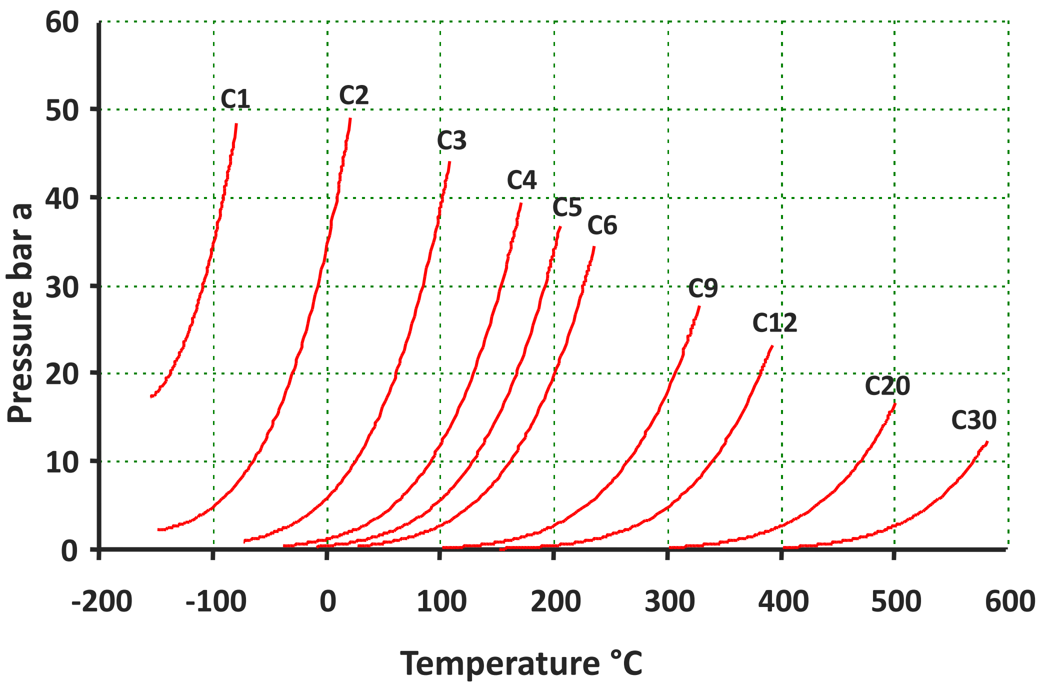
Pure component equilibrium



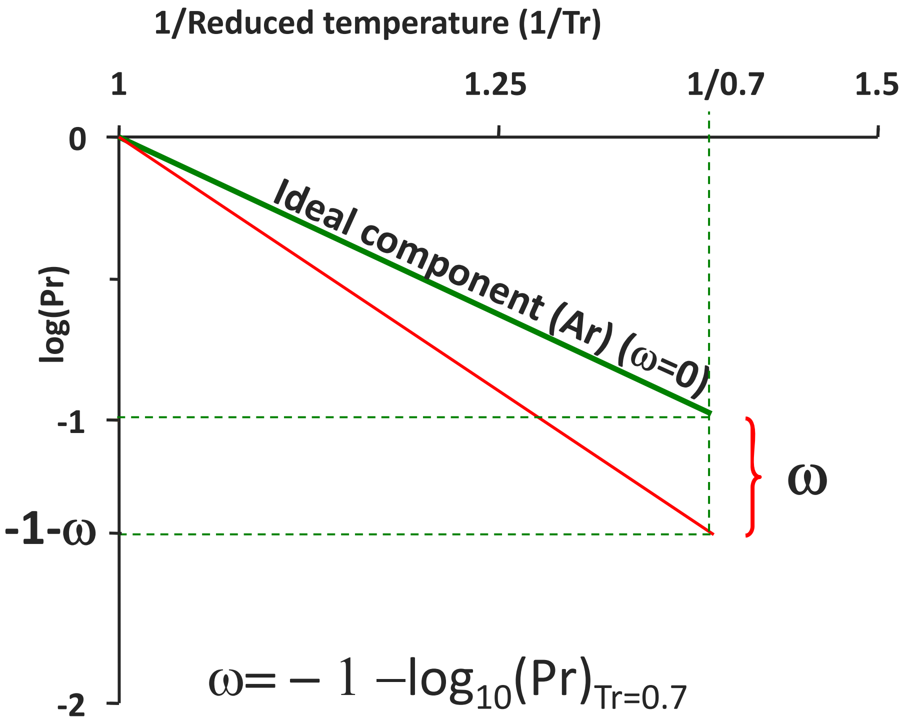
Vapor pressure curve of C2H6



Vapor pressure curves of several normal alkanes



Acentric factor w



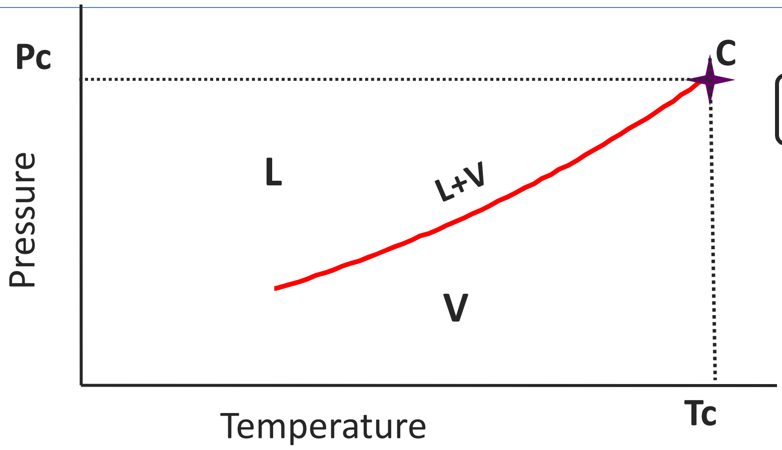
$$\omega = -1 - \log_{10}(Pr)_{Tr=0.7}$$

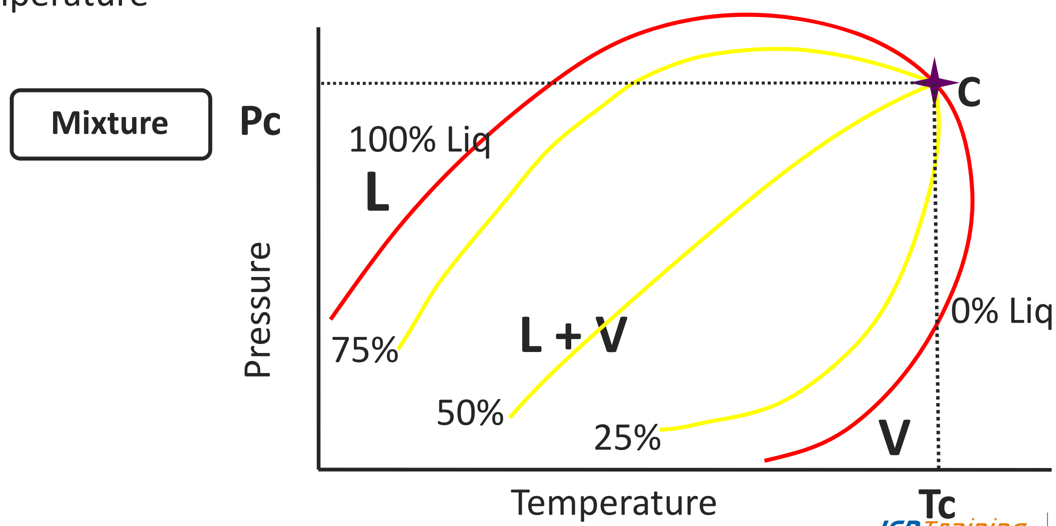
(Pitzer's factor)

Properties of pure components

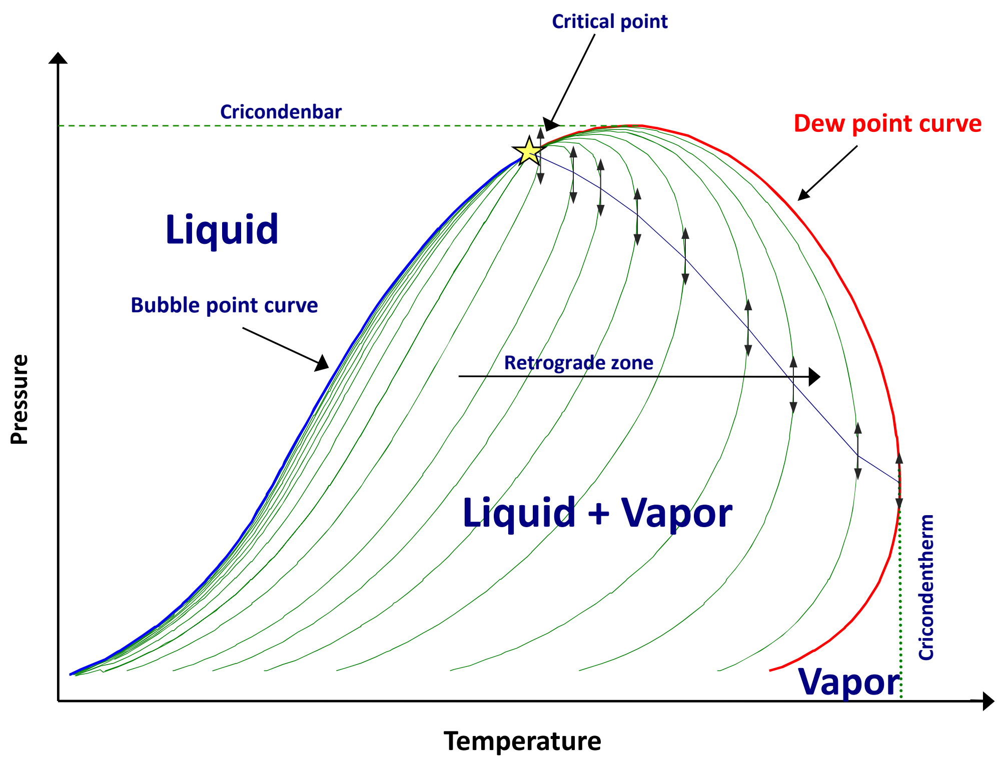
Name	Mw (g/gmol)	Tc (K)	Pc (bar)	Acentric factor
methane	16.04	190.4	46.0	0.011
ethane	30.07	305.4	48.8	0.099
propane	44.10	369.8	42.5	0.153
n-butane	58.12	425.2	38.0	0.199
i-butane	58.12	408.2	36.5	0.183
n-pentane	72.15	469.7	33.7	0.251
i-pentane	72.15	460.4	33.9	0.227
n-hexane	86.18	507.5	30.1	0.299
benzene	78.11	562.2	48.9	0.212
cyclohexane	84.16	553.5	40.7	0.212
n-heptane	100.20	540.3	27.4	0.349
n-octane	114.23	568.8	24.9	0.398
n-nonane	128.26	594.6	22.9	0.445
n-decane	142.29	617.7	21.2	0.489
nitrogen	28.01	126.2	33.9	0.039
carb dioxoyde	44.01	304.1	73.8	0.239
hydr sulfide	34.08	373.2	89.4	0.081

Liq-Vap equilibrium

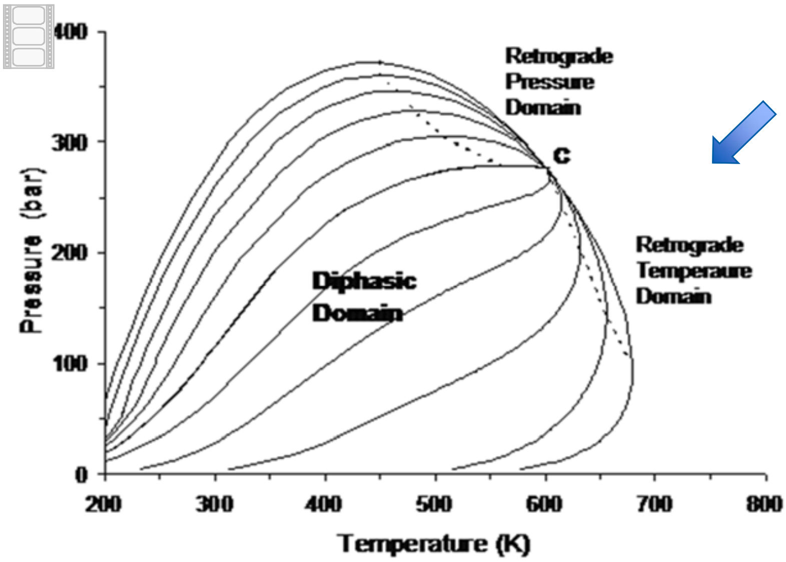




Phase envelope

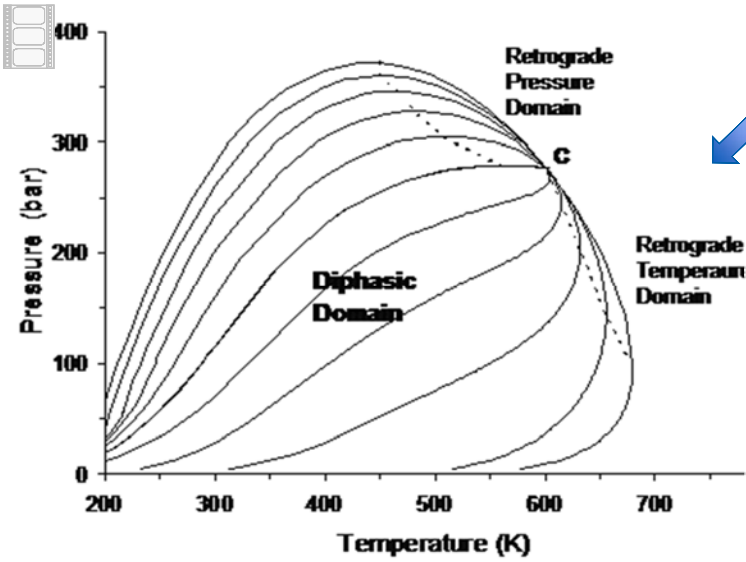


Phase envelope

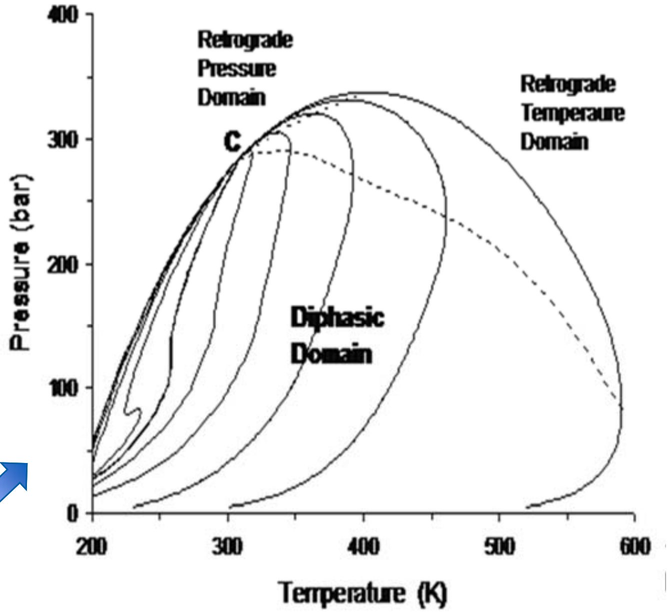


Liquid like

Phase envelope

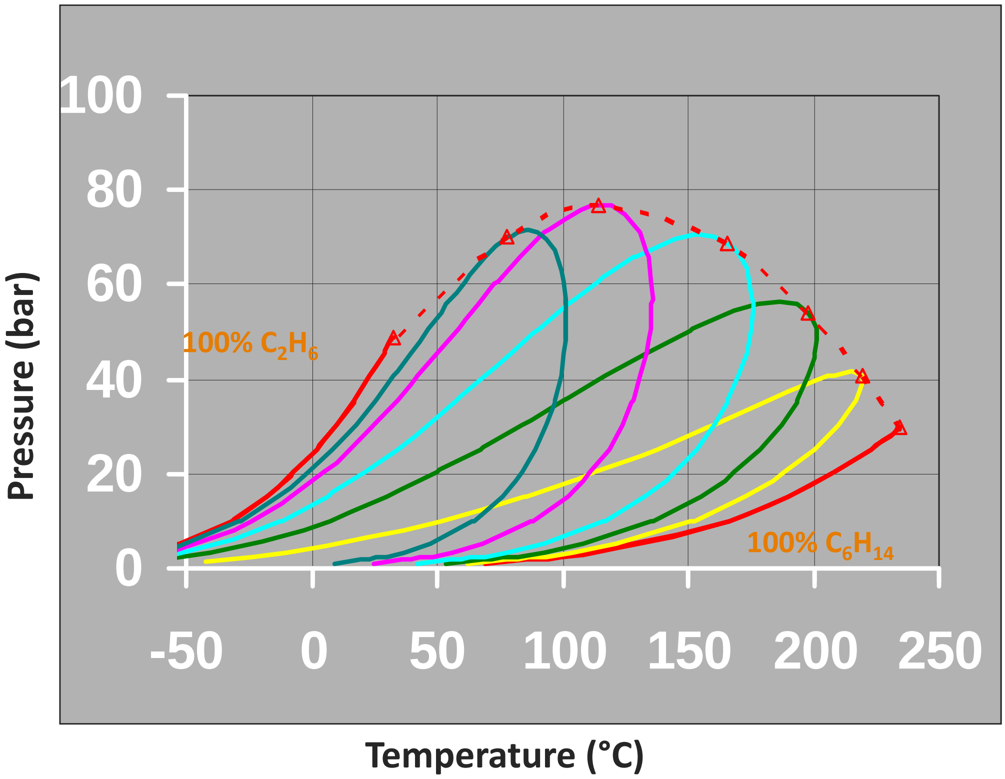


Liquid like



Gas like

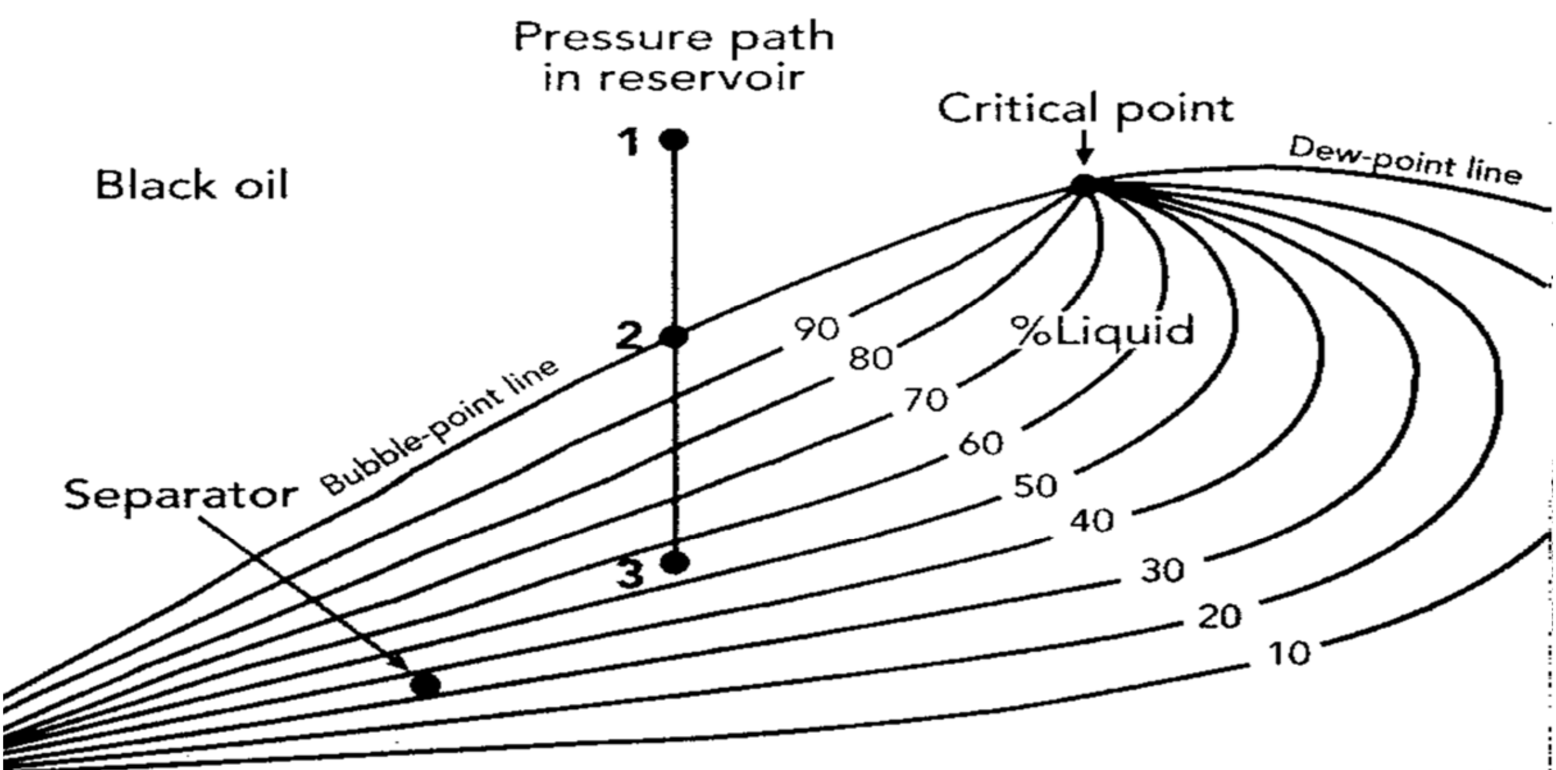
C_2H_6 - C_6H_{14} binary mixtures



Hydrocarbon fluid classification

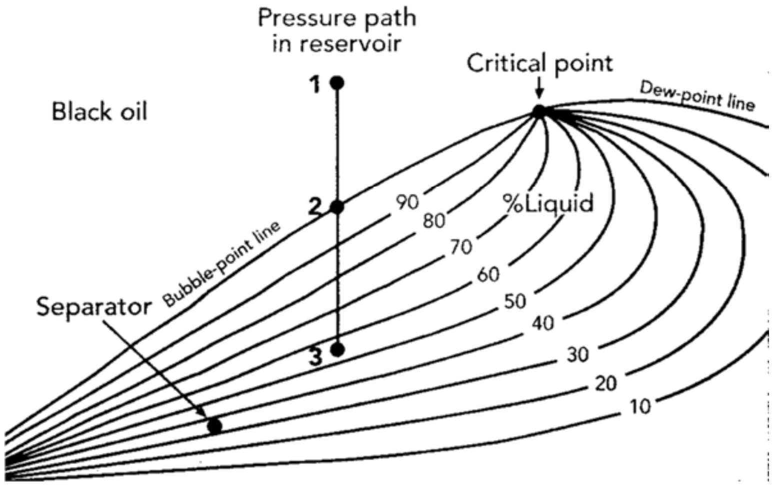
Summary

Under saturated oil

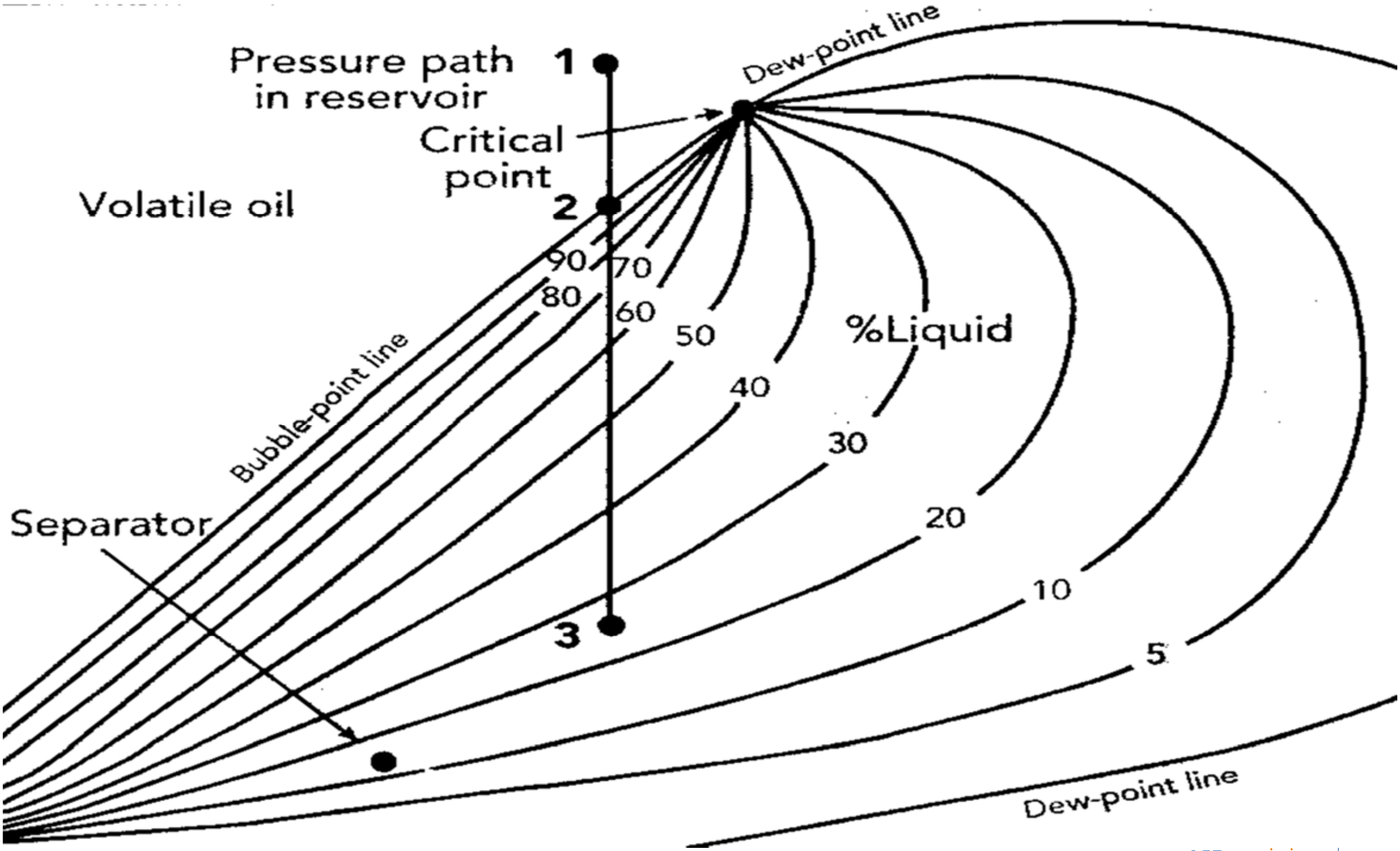


Under saturated oil

- Point 1 indicates that the initial reservoir pressure is undersaturated.
- As reservoir depletion proceeds from 1 to 2, reservoir hydrocarbon fluid moves in the pore space in the form of single phase oil and gas-oil ratio (the ratio of gas produced at surface conditions to the oil produced at surface conditions) at surface conditions is constant. The amount of oil production necessary to bring the pressure down from point 1 to 2 is a small fraction of the total production.
- As production continues and pressure is reduced along path 2 to 3, gas comes out of solution in the reservoir.
- At point 3, the effective permeability to oil and gas are about equal.
- But the viscosity of the oil is about two-orders of magnitude larger than viscosity of the gas.
- Therefore, at point 3, usually more than 90% of the reservoir flow stream volume is gas.

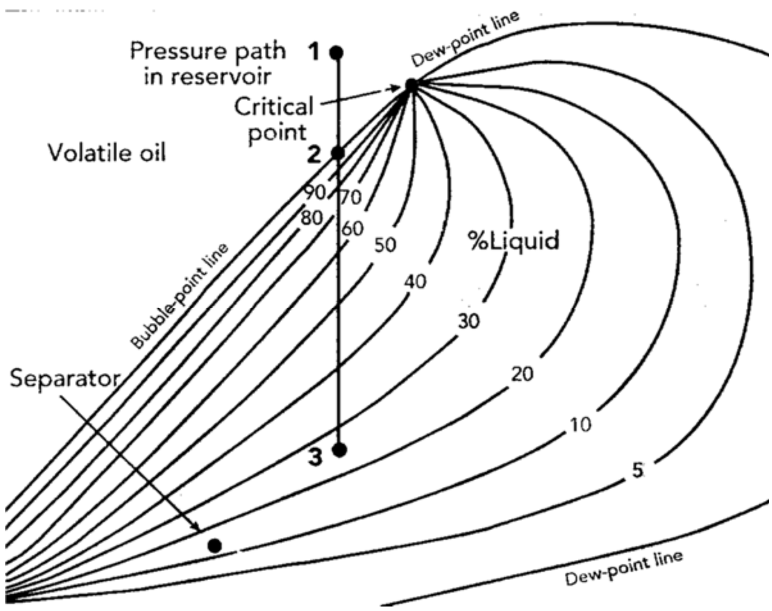


Volatile oil

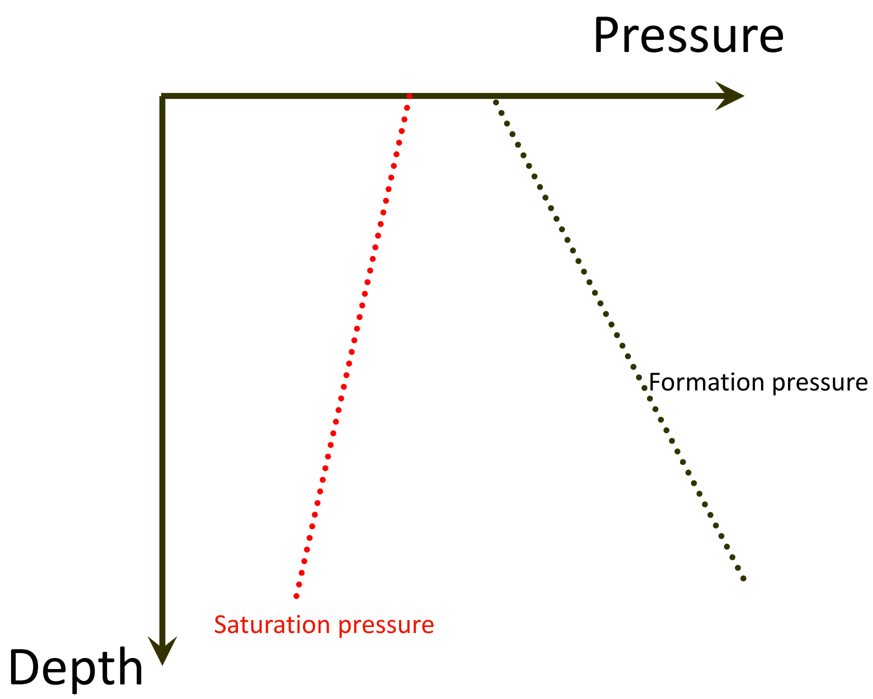


Volatile oil

- Volatile oils have fewer heavy molecules than black oils.
- The critical temperature of volatile oil is much lower than that of black oil, and is close to reservoir temperature.
- The figure on the left shows that, as reservoir pressure is reduced below bubble point pressure, large volumes of gas leave the solution.
- This rapidly reduces the effective permeability to oil and the reservoir flow stream becomes mostly gas within a few hundred psi below the bubble point.
- The effective permeability to oil may become virtually zero and the flow stream may essentially be gas long before reservoir reaches the point 3.

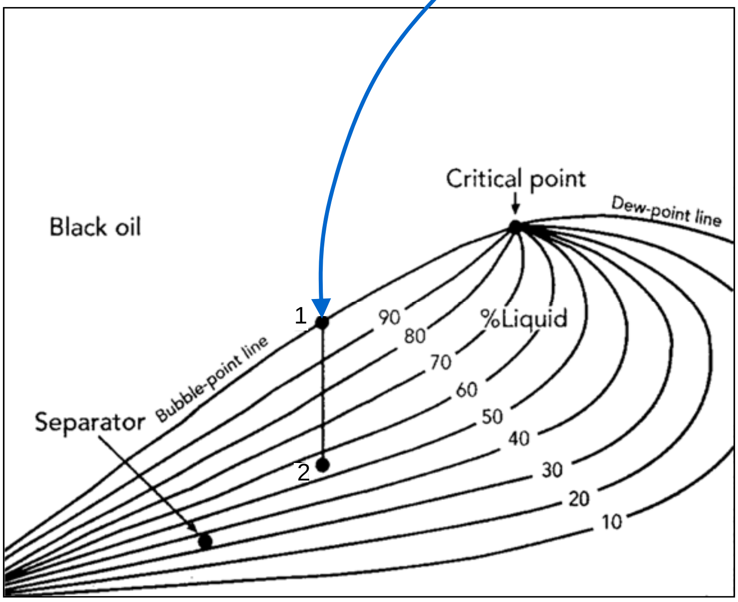


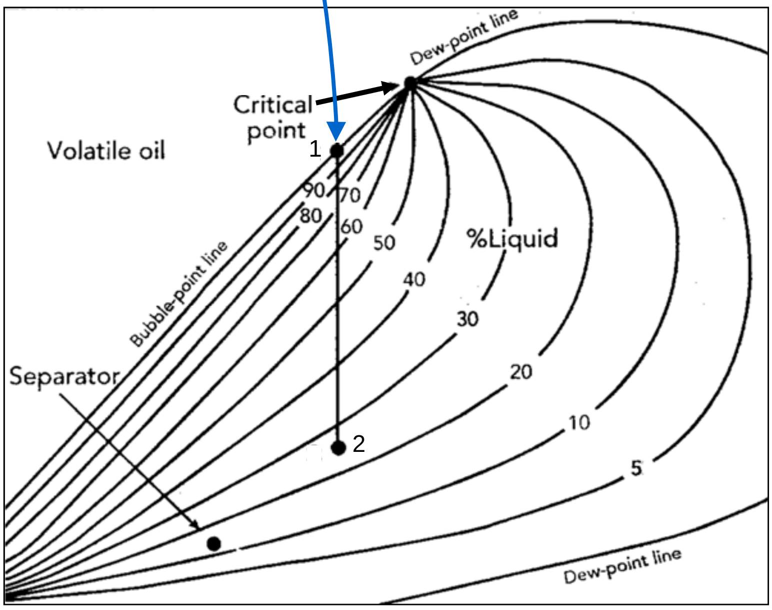
Under saturated oil



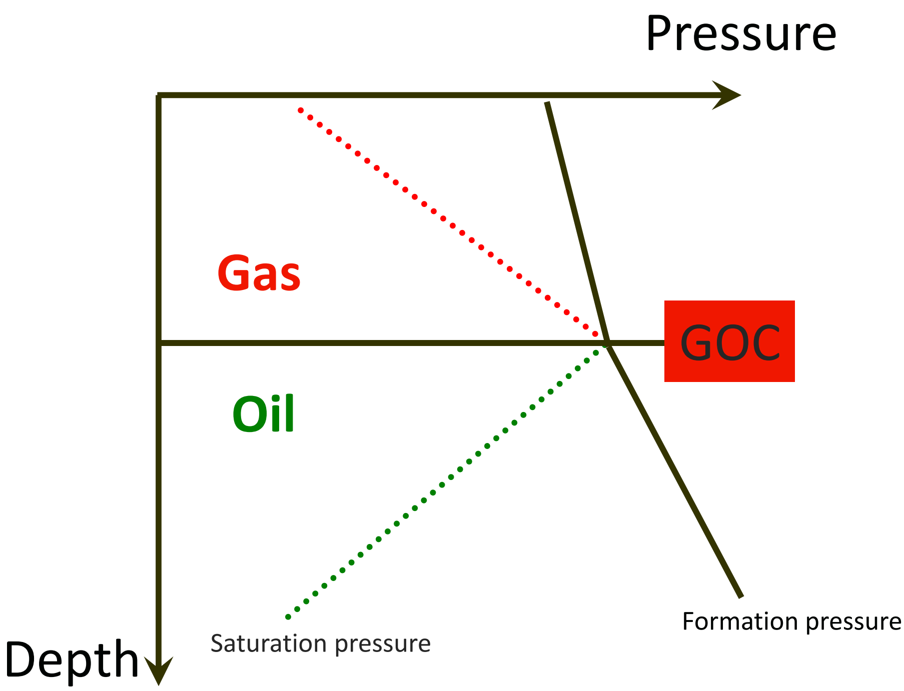
Saturated oil

Saturated oils

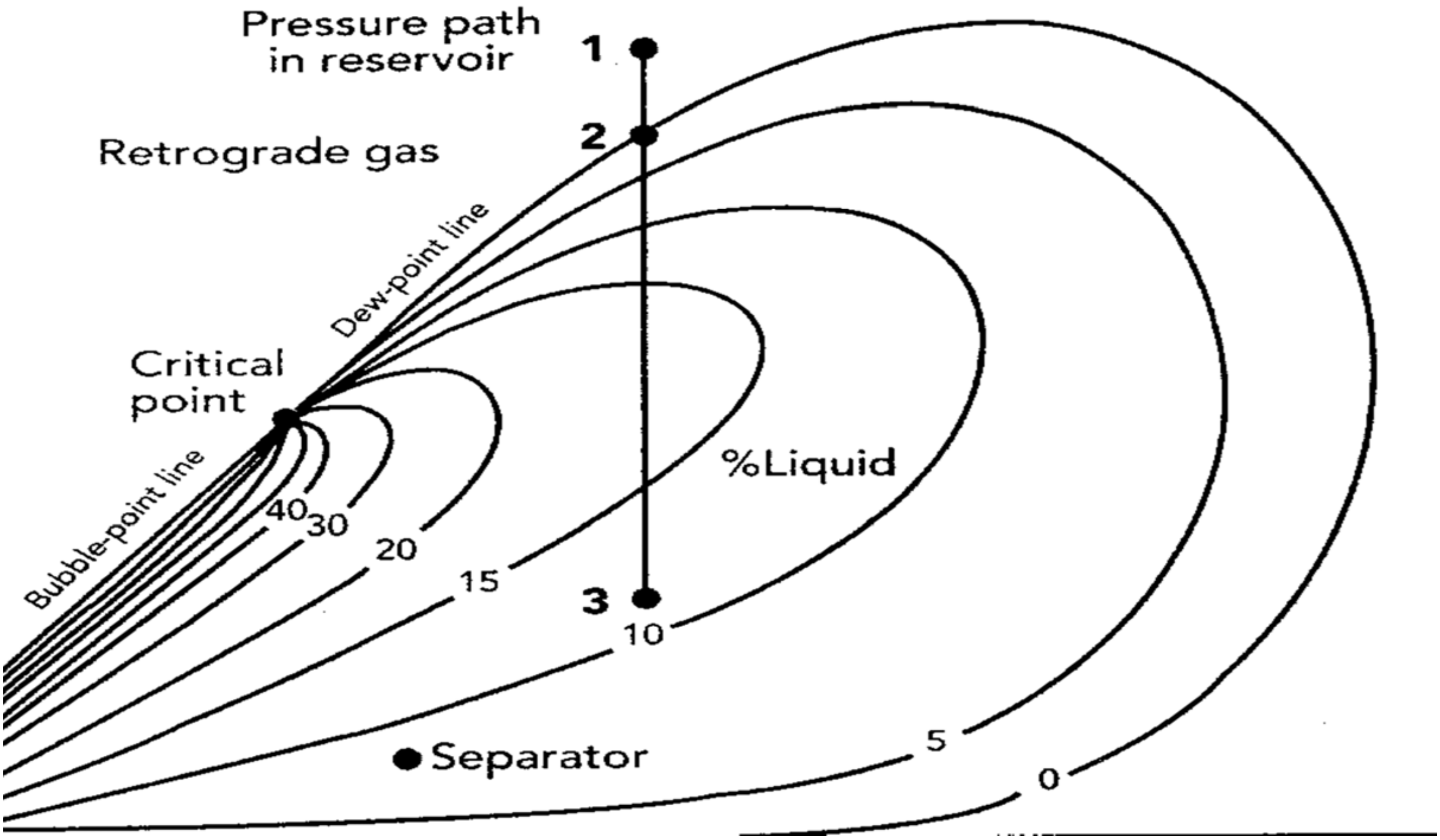




Saturated oil

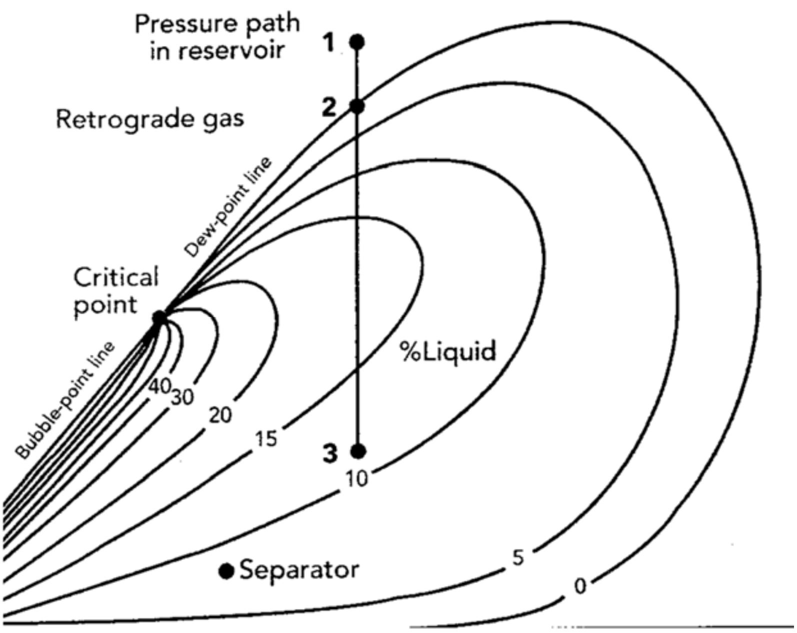


Condensate gas

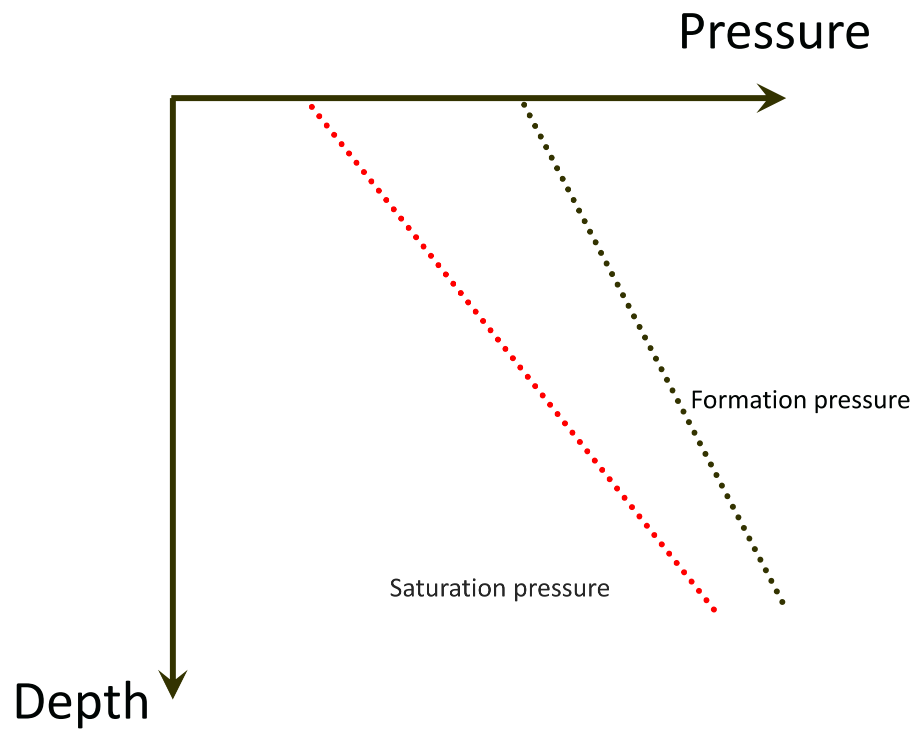


Condensate gas

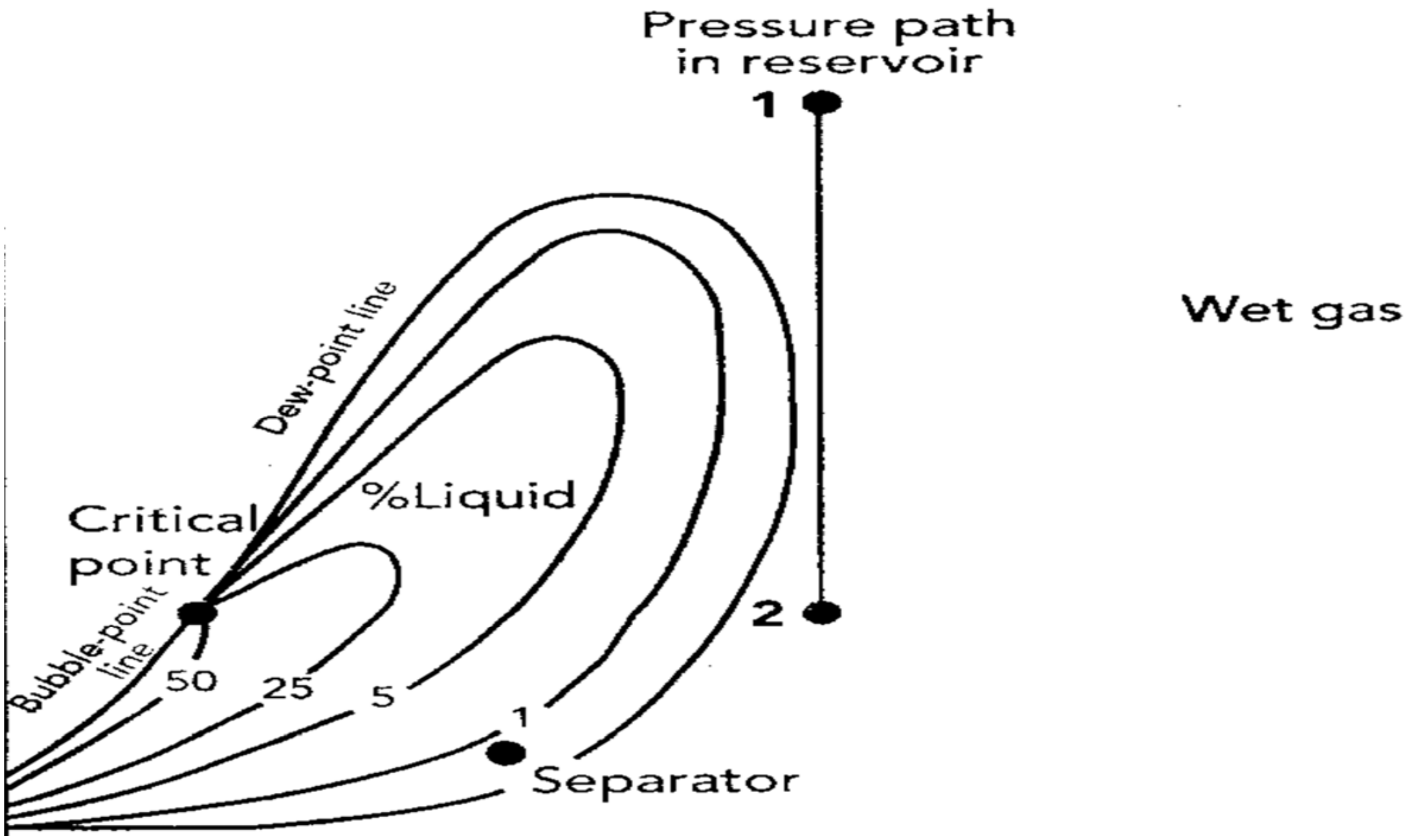
- Retrograde gases have even fewer heavy molecules than volatile oils.
- The critical point shifts to the left and downward in the phase diagram and the critical temperature is usually less than reservoir temperature.
- Retrograde condensate appears in the reservoir pore spaces at pressure below the dew point pressure. Throughout most of the reservoir, since the amount of liquid in the pore space is usually smaller than critical oil saturation the effective permeability to this condensate is zero and little is produced.
- Along line 2 to 3, the condensate builds up first and then revaporizes at the lower pressures.
- This behavior is typical for constant composition expansion type application.
- At reservoir conditions can we see re-evaporation?



Condensate gas

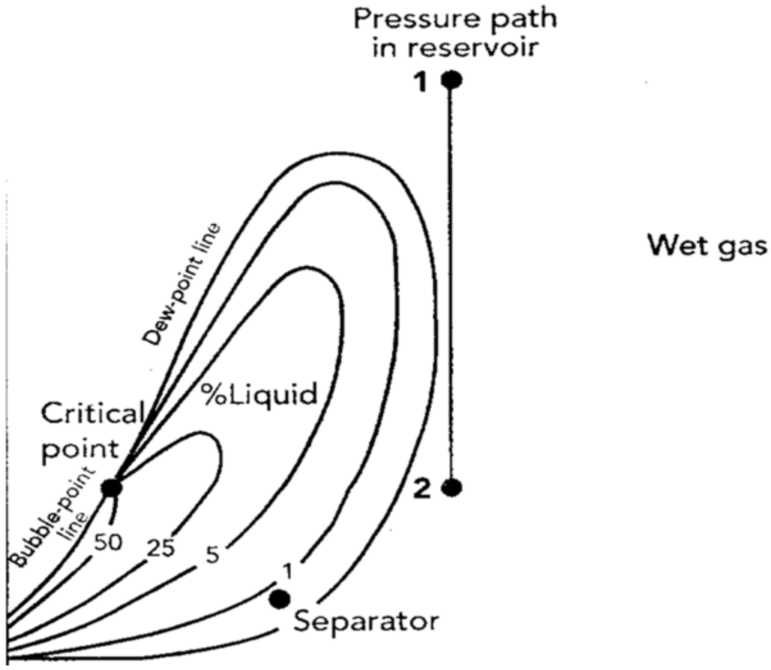


Wet gas

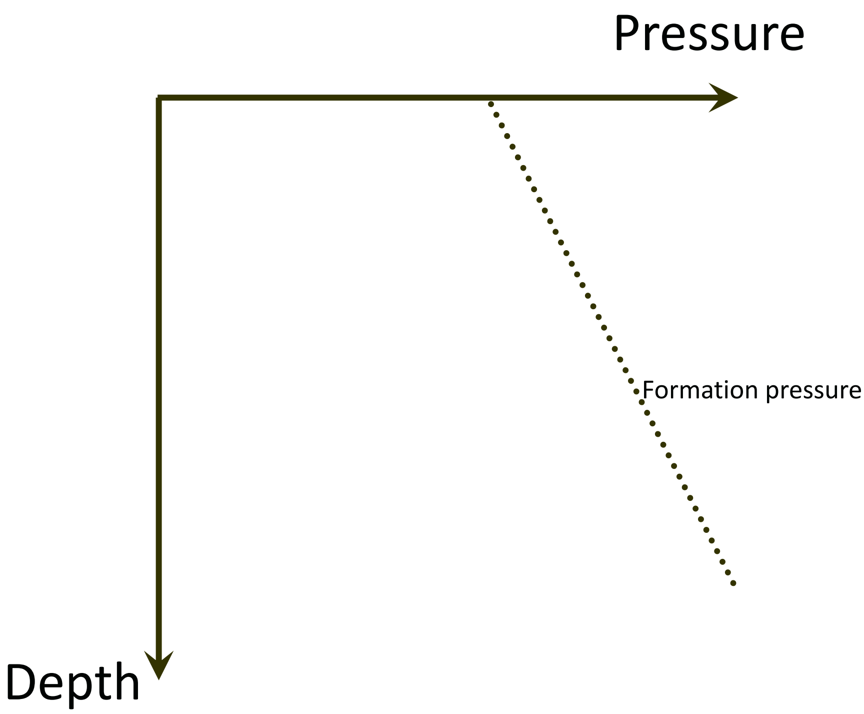


Wet gas

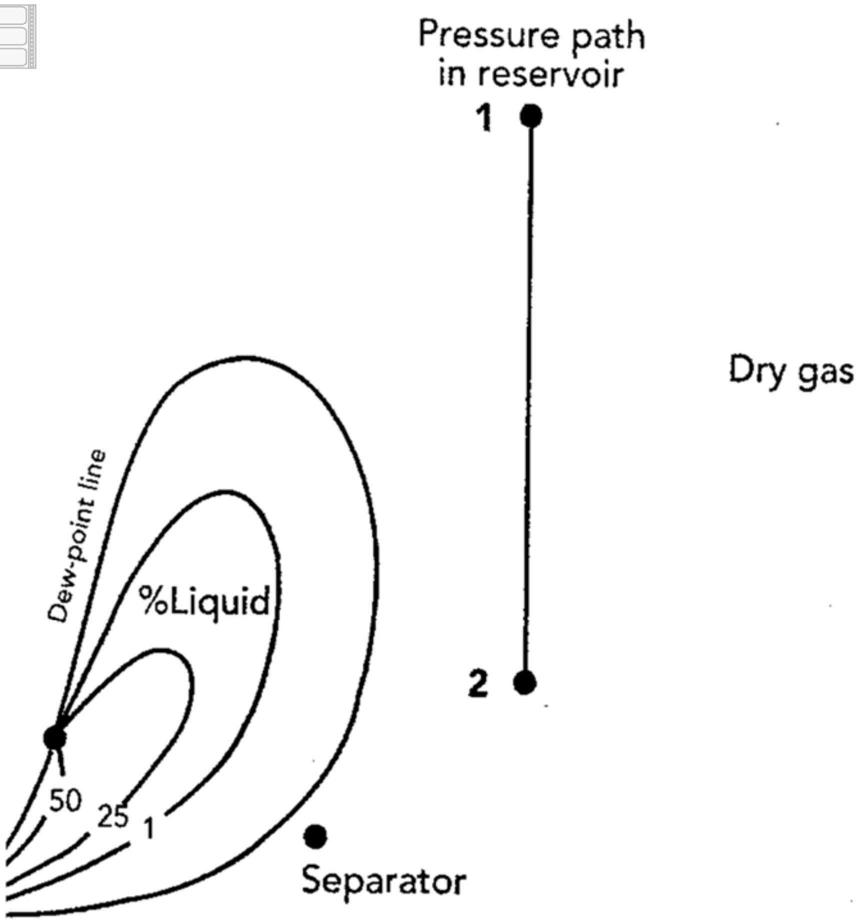
- The composition of a wet gas contains much fewer heavy molecules.
- Because the phase diagram covers a much smaller temperature range, the pressure depletion path in the reservoir does not enter the two-phase region.
- The reservoir fluid is gas throughout the life of the reservoir.
- However, separator conditions lie within the two-phase envelope, indicating that some liquid will condense at the surface



Wet gas

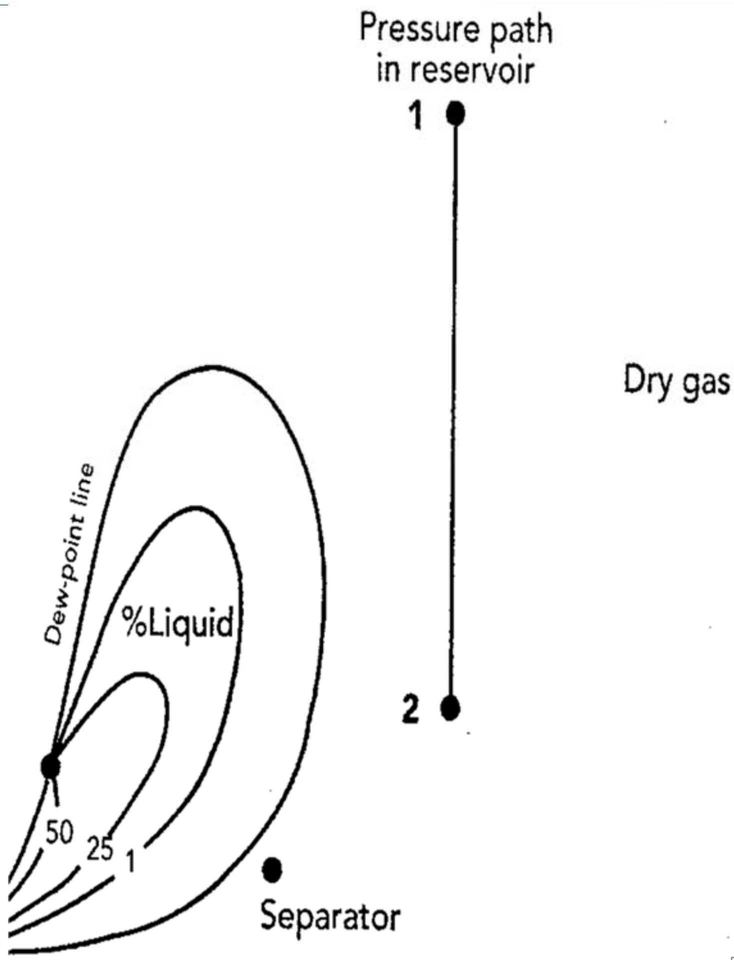


Dry gas

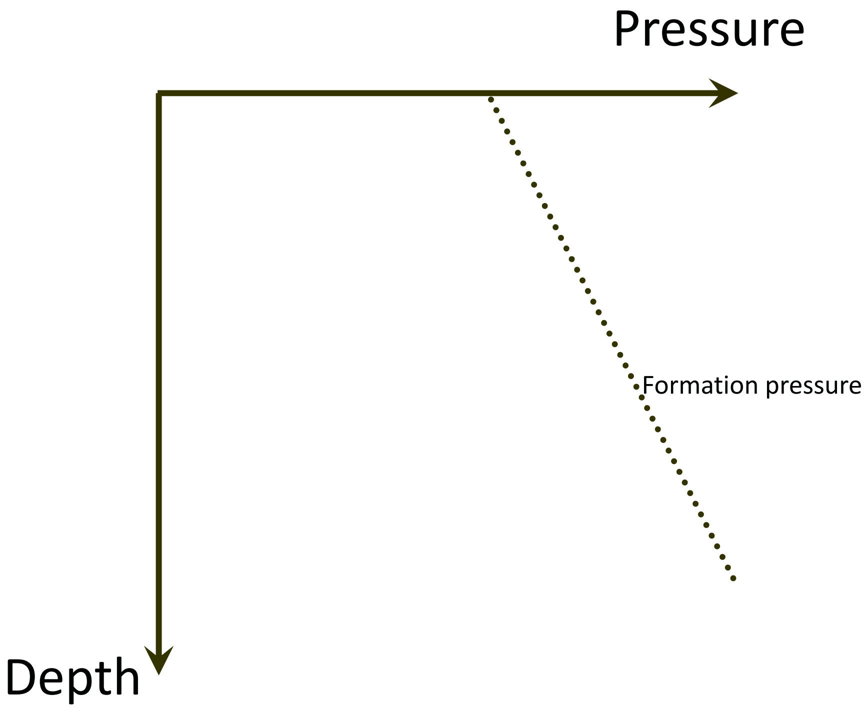


Dry gas

- Dry gas is virtually pure methane.
- The two-phase envelope is small and lies below reservoir conditions and to the left of surface condition
- The fluid is theoretically gas both in the reservoir and at the surface.



Dry gas



Fluid classification

CF: Critical Fluid

GC: Condensate Gas

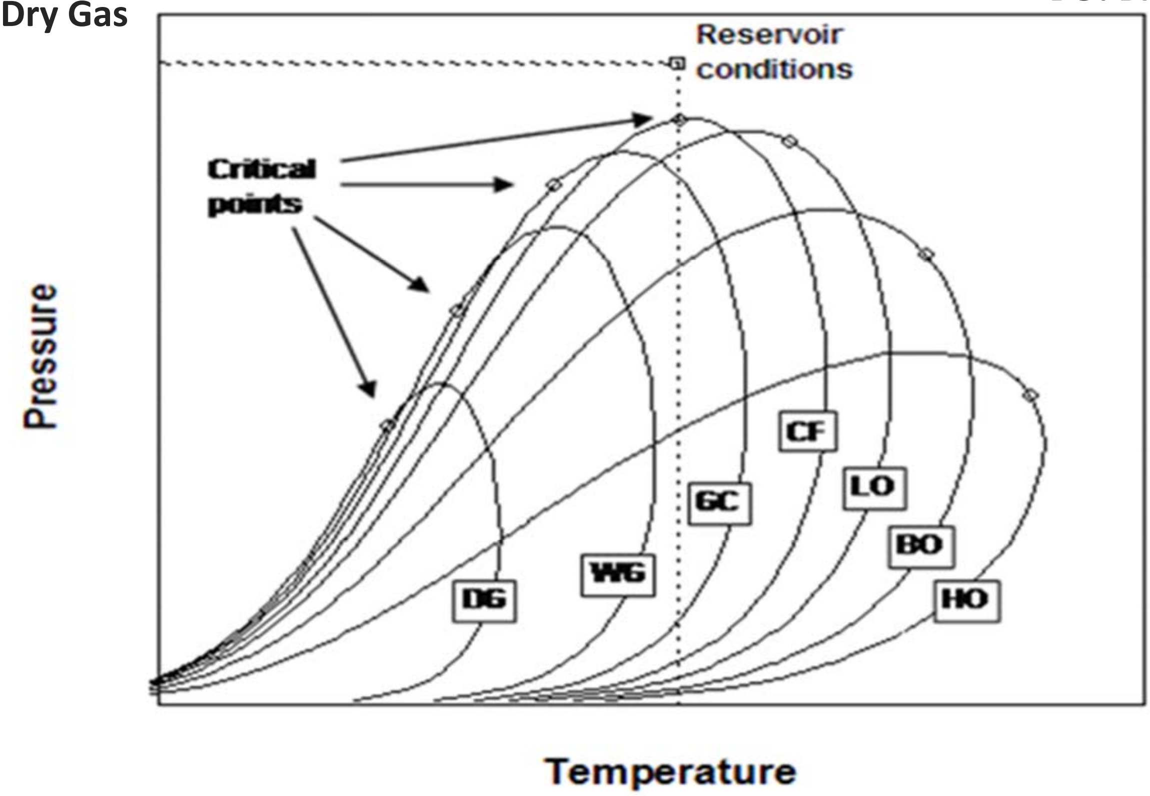
WG: Wet Gas

DG: Dry Gas

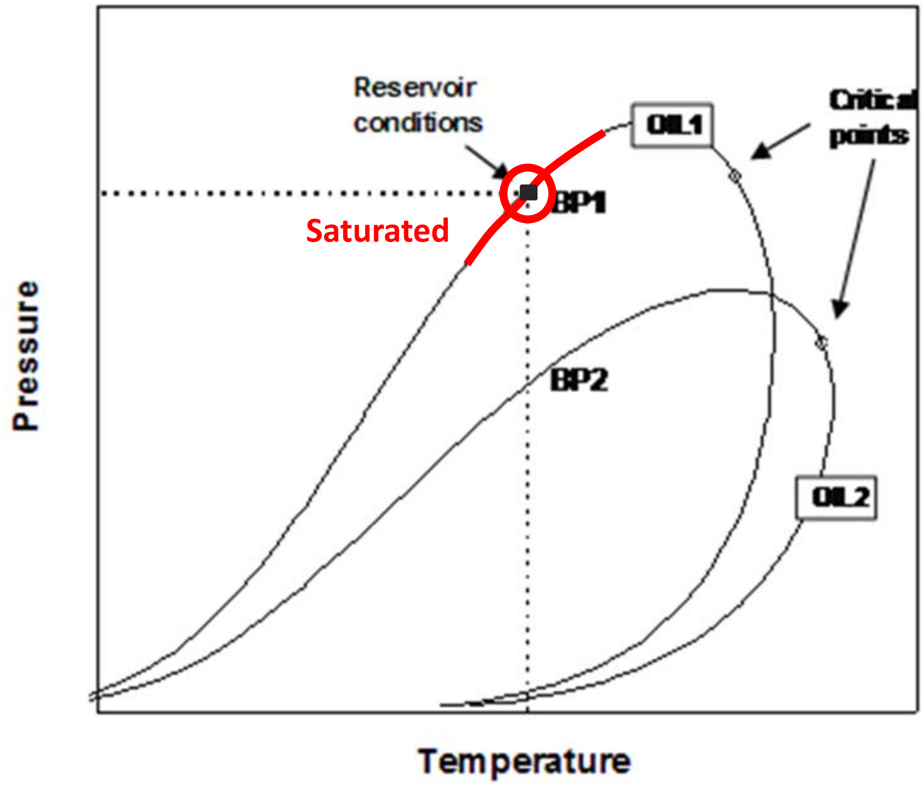
LO: Light Oil

BO: Black Oil

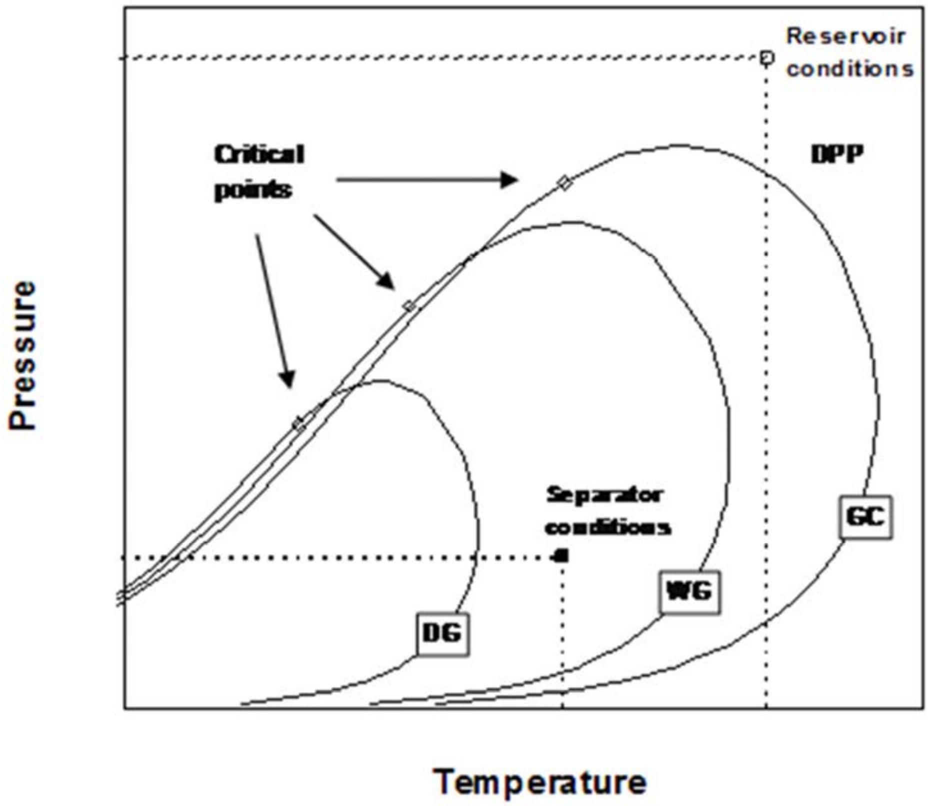
HO: Heavy Oil

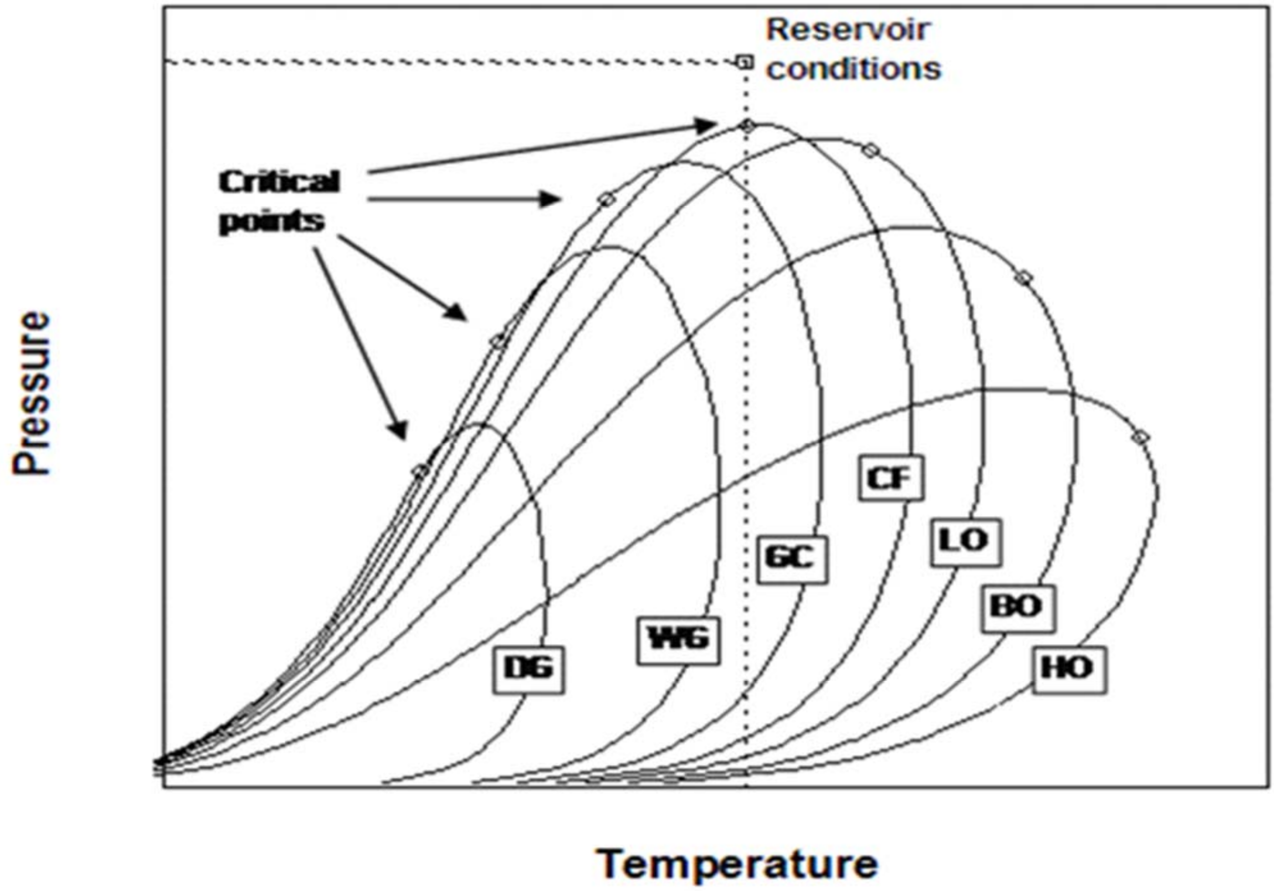


Fluid classification: saturated or not



Fluid classification: gases





Well test	Separator GOR (Sm³/m³)	Density of STO (kg/m³)	Composition (mole %) C1	C2	C3	C4	C5	C6+
Heavy oil	< 10	> 900		3	4	5	8	80
Standard oil	< 500	800 - 900	45	4	4	3	2	42
Critical fluid	# 700	750 - 850	55	10	8	5	6	16
Condensate gas	700 - 800	700 - 800	75	8	5	2	2	8
Wet gas	> 15000	700 - 800	90	5	3	1	1	1
Dry gas	infinite		95	3	1	1		

Well test	Separator GOR (Sft³/barrel)	Density of STO (lb/ft³)	Composition (mole %) C1	C2	C3	C4	C5	C6+
Heavy oil	< 60	> 56		3	4	5	8	80
Standard oil	< 3000	50 - 56	45	4	4	3	2	42
Critical fluid	# 4000	47 - 53	55	10	8	5	6	16
Condensate gas	4000-4500	47 - 53	75	8	5	2	2	8
Wet gas	> 85000	44 - 50	90	5	3	1	1	1
Dry gas	infinite		95	3	1	1		

Bottomhole properties

Well test	GOR separator (Sm^3/m^3)	Bottomhole density (kg/m^3)	Bottomhole Viscosity (**) (cPo)
Bitumen		> 950	> 1000
Heavy oil	< 10	850 - 950	sevl 10^2 to sevl 10^3
Standard oil	< 500	550 - 850	0.2 to several
Critical fluid	# 700	450 - 550	0.2 to several
Gas condensate	700 - 800	300 - 450	< 0.3
Wet gas	> 15000	100 - 400 (*)	< 0.3
Dry gas	infinite	100 - 400 (*)	< 0.3

*: highly pressure-dependent

**: highly temperature-dependent

?

Evolution of density and viscosity		
Single-phase (P > P sat)		***ρ and μ vary with P***
Two-phase (P < P sat)	Oil	***ρ and μ vary contrary to P***
	Gas	***ρ and μ vary with P***

Oil and gas specific gravity

Stock Tank Oil Specific Gravity

- **API definition: ° API = (141.5 / SG) - 131.5**
  SG being the specific gravity of oil w.r.t water @ 60°F
  - Condensates, very light oil — SG < 0.8 (> 45°API)
  - Light oil — 0.80 < SG < 0.86 (33-45°API)
  - Standard oil — 0.86 < SG < 0.92 (22-33°API)
  - Heavy oil — 0.92 < SG < 1.00 (< 22°API)

Gas Specific Gravity

- **Gas SG is defined w.r.t air @ Std conditions (60°F, 1 atm).**
- **Gas SG can be determined from the gas composition (Mw):**
  SG = (gas Mw) / (air Mw) with air Mw = 28.996 g/gmol
- **SG = Mw / 29**

PVT Experiments

- **Oils – Condensate gases**

Summary

PVT experiments

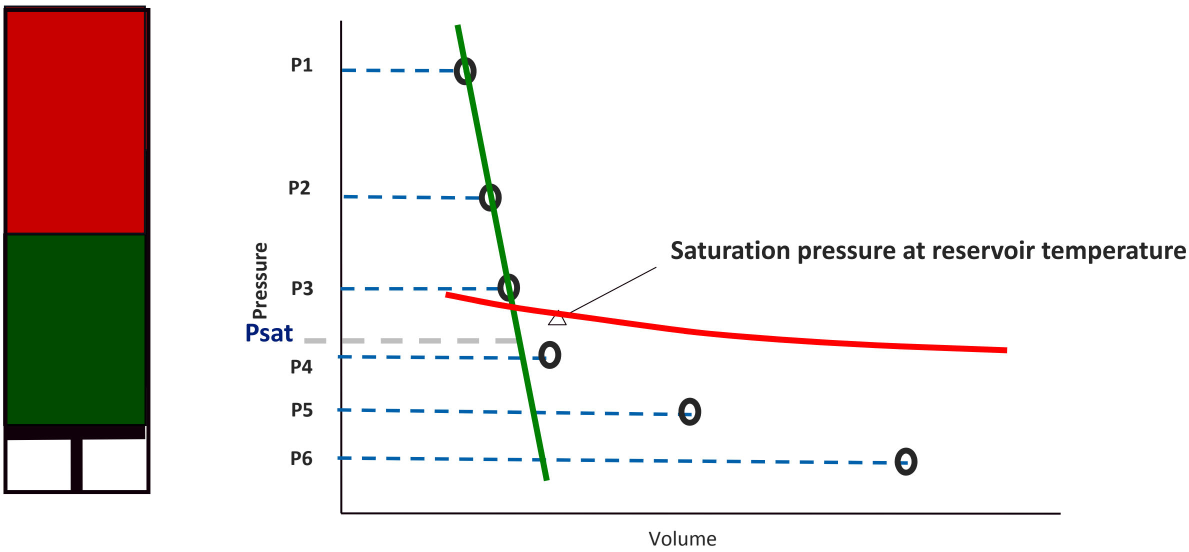
- **Oil:**
  - Bubble point
  - Flash test
  - Multi stage separation
  - Differential liberation
  - Constant Mass Expansion (CME)
  - Viscosity under pressure

- **Gas:**
  - Dew point
  - Multi stage separation
  - Constant Mass Expansion (CME)
  - Constant Volume Depletion (CVD)

PVT experiment:

constant mass expansion for an oil

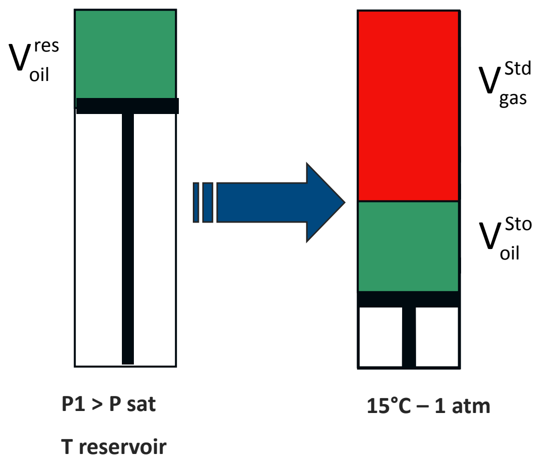
Graphical determination of the saturation pressure



PVT experiment: flash test for an oil

- **Objective:**
  - To determine reservoir fluid composition

- **Main properties derived from this experiment:**
  - Molecular composition of reservoir fluid
  - Rough GOR value
  - Rough Bo value
  - Density and viscosity of oil at atmospheric conditions



$$Bo = \frac{V_{oil}^{res}}{V_{oil}^{Sto}} \qquad GOR = \frac{V_{gas}^{Std}}{V_{oil}^{Sto}}$$

PVT experiment: flash test for an oil

Characterization of oil and gas phases

Gas

- **Composition (GC)**
- **% H_2S**
- **Trace components**
- **SG**

Oil

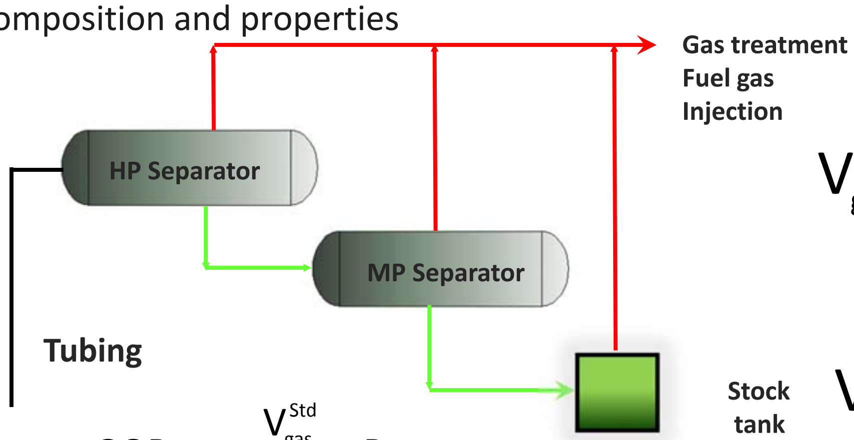
- **Composition (GC)**
- **Heavy fraction (GPC)**
- **Wax**
- **WAT**
  Wax Appearance Temperature
- **Pour point**
  Lowest Flowing Temperature
- **Density**
- **Viscosity**

PVT experiment: multi stage test for an oil

- **Objective:**
  - Simulation of field test or process separation scheme
- **Main properties derived from this experiment:**
  - GOR
  - Process Rsi
  - Process Boi
  - Gas composition at each step
  - Stock tank liquid composition and properties

$$GOR_{Sep} = \frac{V^{Std}_{gas\text{-}sep}}{V^{Sep}_{oil\text{-}sep}}$$

V^{res}_{oil}



V^{Std}_{gas}

V^{Sto}_{oil}

$$Bo = \frac{V^{res}_{oil}}{V^{Sto}_{oil}}$$

$$GOR_{Total} = \frac{V^{Std}_{gas}}{V^{Sto}_{oil}} = R_s$$

PVT experiment: multi stage test for an oil

Characterization of oil and gas phases

Gas

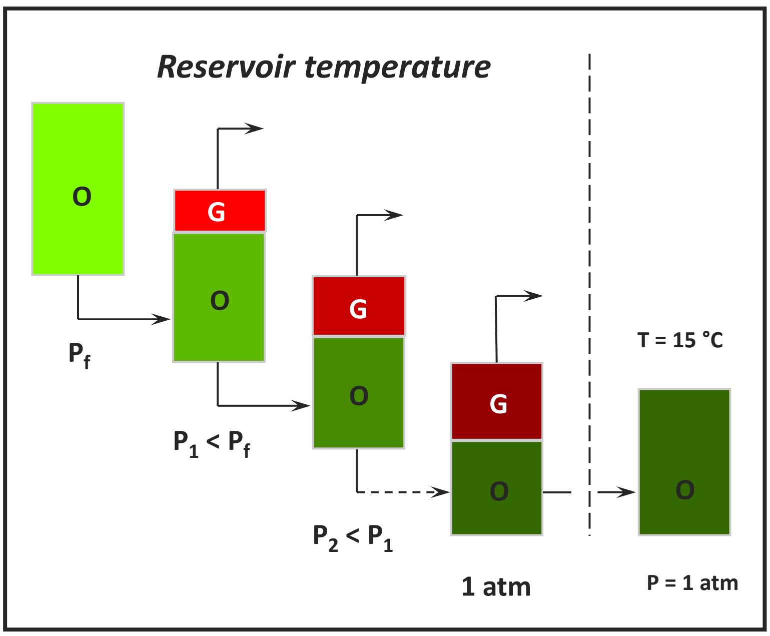
- Composition (GC)
- % H_2S
- Trace components
- SG

Oil

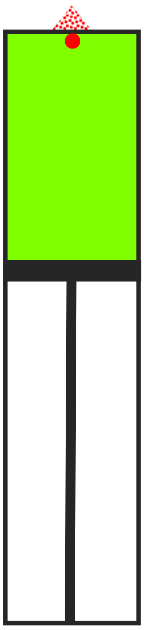
- Composition (GC)
- Heavy fraction (GPC)
- Wax
- WAT
- Pour point
- Density
- Viscosity

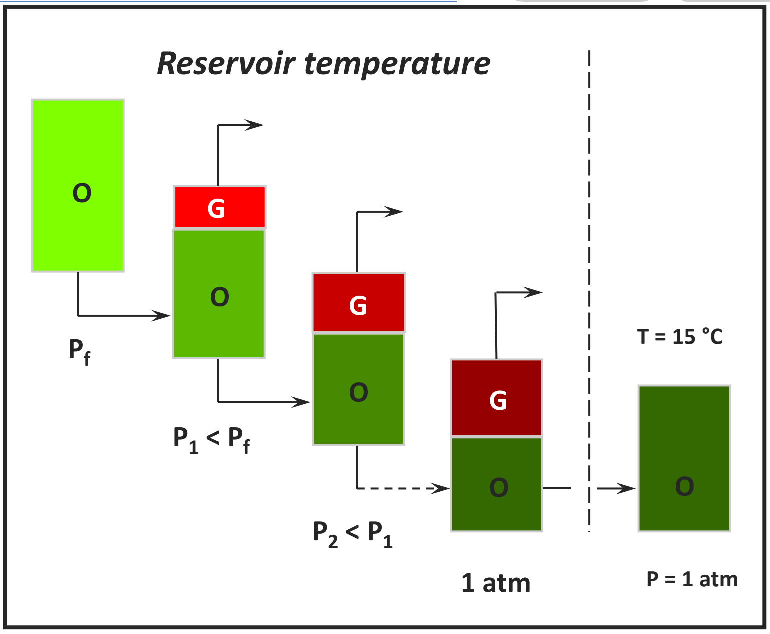
PVT experiment: differential liberation for an oil

- **Objective:**
  - Simulation of reservoir depletion
- **Main properties derived from this experiment:**
  - Liberation GOR
  - Differential Rsb
  - Differential Bob
  - Gas composition at each step
  - Residual oil composition and properties



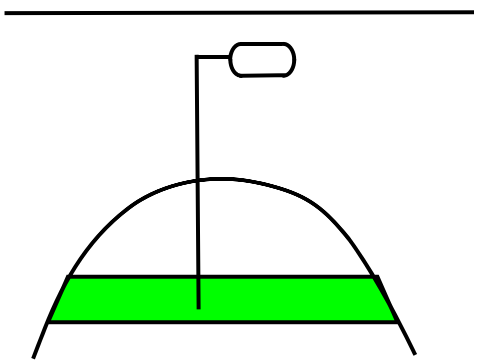
Differential vaporization





$$Bg = \frac{V_{gas}^{P_i}}{V_{gas}^{Std}} \qquad Bo = \frac{V_{oil}^{P_i}}{V_{oil}^{Sto}} \qquad GOR_{Total} = \frac{V_{gas}^{Std}}{V_{oil}^{Sto}} = R_s$$

Differential vaporization



Reservoir Pressure

>

Bubble point pressure

No compositional change

Differential vaporization versus multi-stage test

- **Differential liberation. The final volume of liquid phase remaining in the cell at standard conditions is called RESIDUAL OIL**

- **Multi-stage test. Oil that results when one m3 or barrel of oil is flashed through a certain surface separator is called STOCK TANK OIL.**

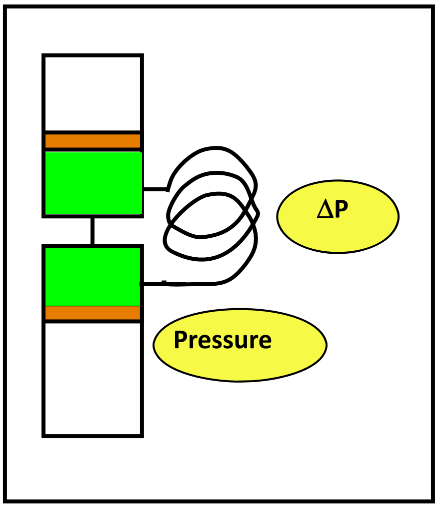
- **RESIDUAL OIL and STOCK TANK OIL are both products of the original oil but are developed by different pressure-temperature routes.**
  - Multiple series of flashes at the elevated temperature of the reservoir
  - Some stage flash at low temperature and pressure

$$B_O^{Dif} > B_O^{Sep} \qquad R_S^{Dif} > R_S^{Sep}$$

$$\rho_{RO}^{Dif} > \rho_{STO}^{Sep}$$

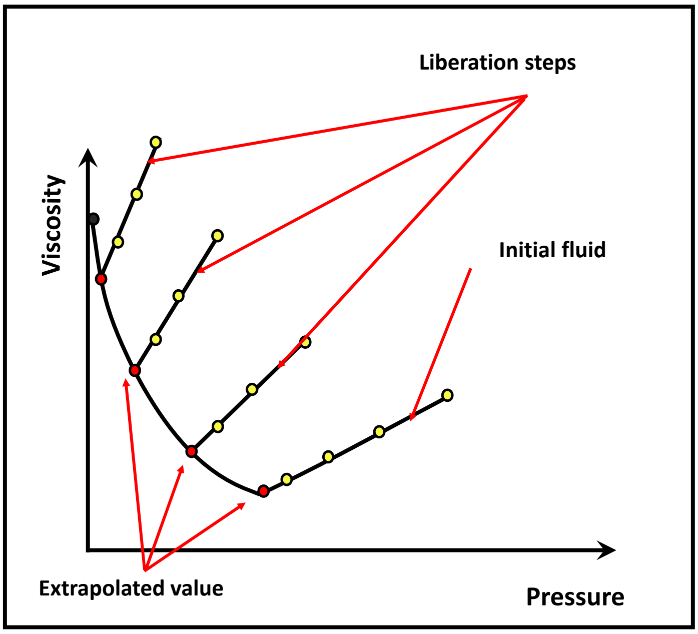
Viscosity measurement

Constant Temperature = reservoir T



Measurement of pressure drop across a capillary tube:

$$\mu = \frac{k.\Delta P}{Q}$$



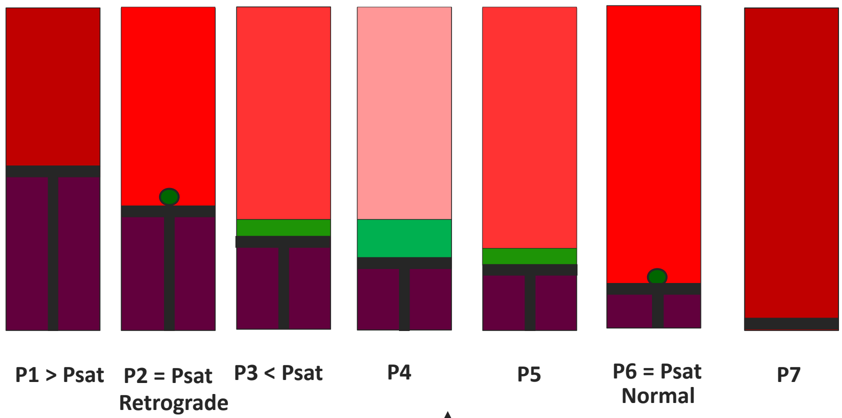
Oil unit performances

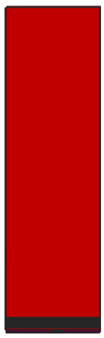
- **Range of work:**
  - Pressure: 1 bar - 1000 bar
  - Temperature: -20°C to 180°C
  - GOR: 5 to 700 m^3/m^3
  - Viscosity: 0.2 to 200 cPo
- **Accuracy:**
  - Volumes:
    - resolution 5 10^{-6} cm^3
    - accuracy 10^{-4} cm^3
  - Temperature: ± 1°C
  - Pressure:
    - HP: ±1 bar
    - BP: $\pm 10^{-3}$ bar
  - Viscosity: $\pm 10^{-2}$ cPo

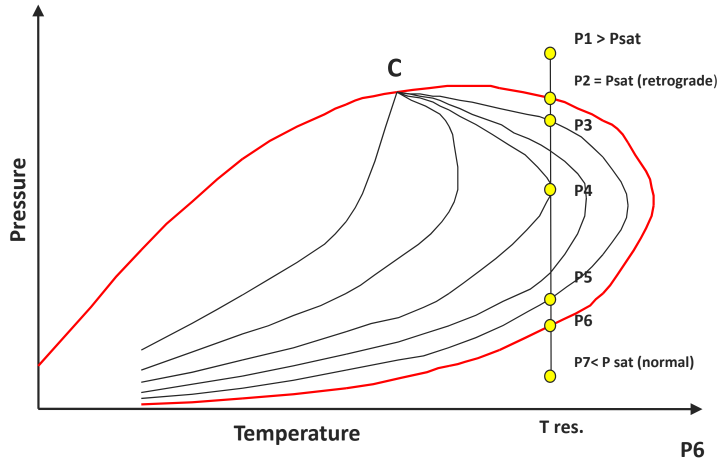
PVT experiment: constant mass expansion for a condensate gas

- **Objective:**
  - Fluid behavior at reservoir conditions
- **Main properties derived from this experiment:**
  - Liquid drop out curve
  - Compressibility factor curve
- **Remarks:**
  - The measurement accuracy of a very small volume of liquid is low.
  - The dew point may never be known better than +/-1.5 bars (20 psi)
- **Notice that CME = CCE**

PVT experiment: constant mass expansion for a condensate gas

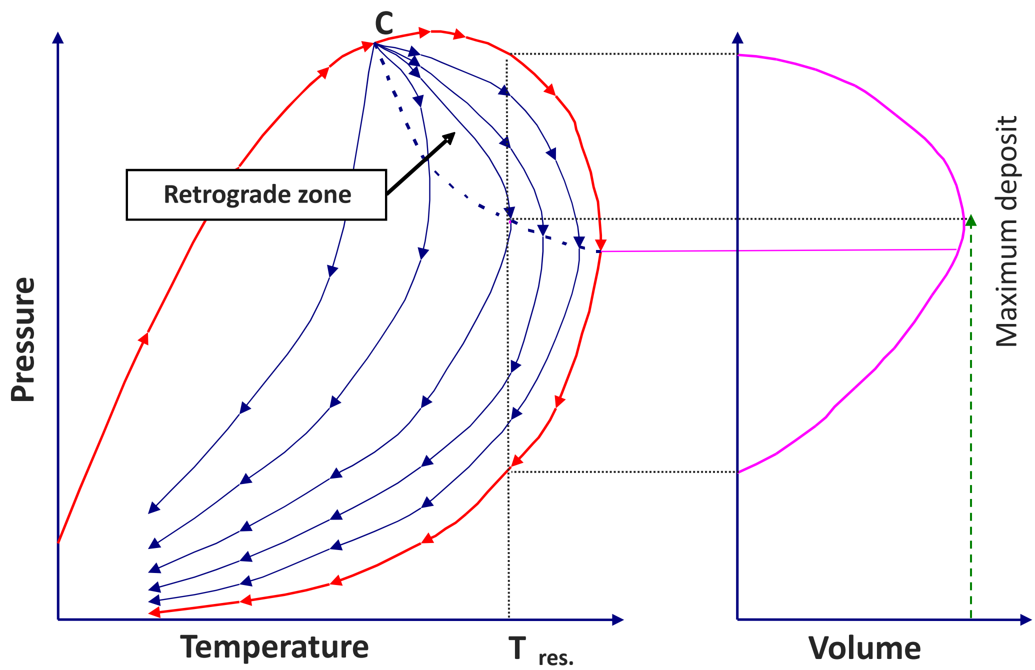




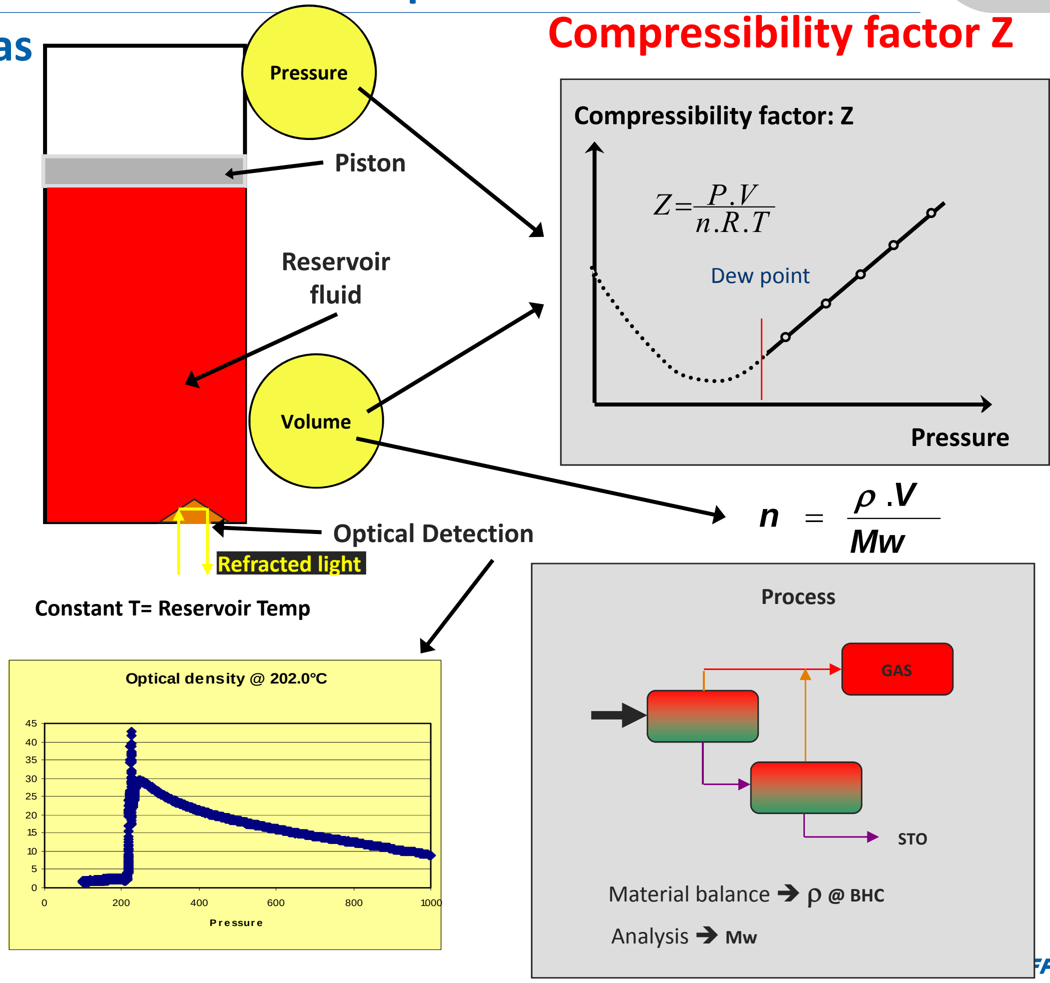


PVT experiment: constant mass expansion for a condensate gas

Phase envelop - Liquid deposit



PVT experiment: constant mass expansion for a condensate gas



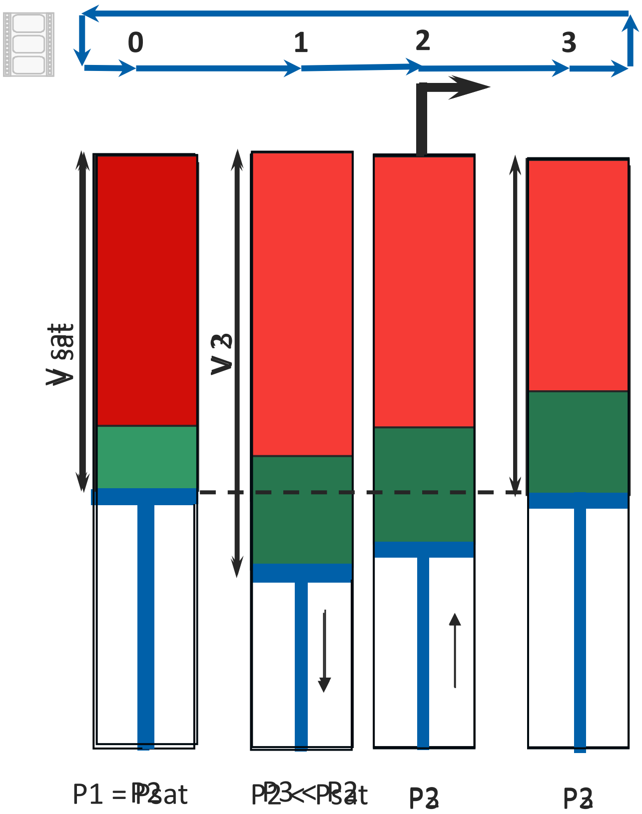
PVT experiment: constant volume depletion for a condensate gas

- **Objective:**
  - Simulation of reservoir production for condensate gas and volatile oil

- **Main properties derived from this experiment:**
  - Liquid drop out curve
  - Volumetric factor of the wellstream during depletion
  - Wellstream composition during depletion

- **Remarks:**
  - Be sure to have vapor and liquid at each step
  - Problems imply negative calculated liquid compositions.
  - Plot Ki(P) = Yi(P) / Xi(P)
    - All lines monotonic and smooth, no crossing, ordered with volatilities
  - Use the Hoffman-Crump-Hocott plot:
    - Log(KiP) is linear regarding B(1/Tbi-1/T) with B=(log(Pci) –log(Pref)) / (1/Tbi-1/Tci)

Constant volume gas depletion



Step by step description

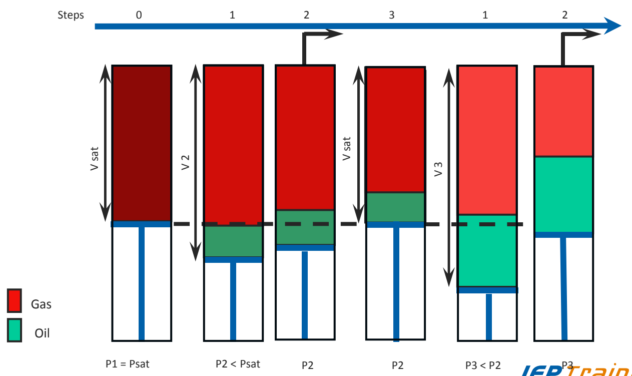
0: Measure reference Volume Vsat à P1=Psat

1: Decrease P to P2<P1 lowering the piston, condensation occurs

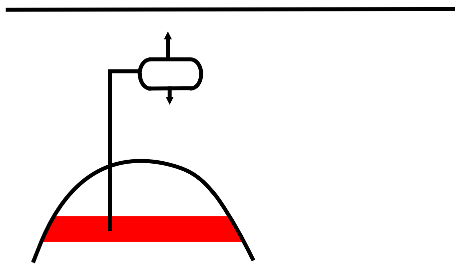
2: Reset the cell volume to Vsat, pushing up the piston

3: Measure Oil and gas volumes

1: Decrease P to P3<P2, …



Constant volume depletion



Current reservoir pressure
>
Dew Point Pressure

Well-stream composition remains unchanged

Liquid deposit is assumed to be not mobile

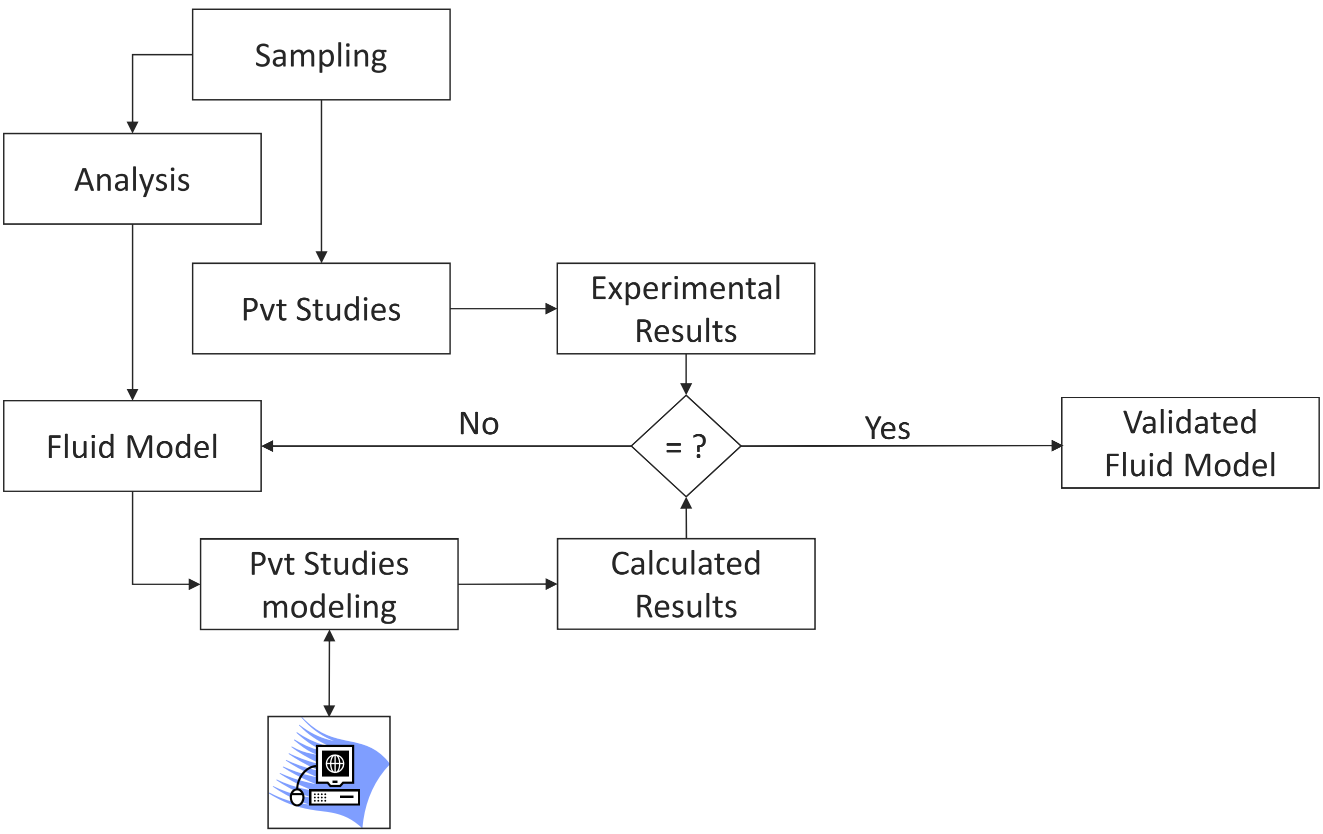
Gas unit performances

- **Range of work:**
  - Pressure: 1 bar - 1500 bar
  - Temperature: -20°C to 200°C
  - Viscosity: 0.05 to 1 cPo
- **Accuracy:**
  - Volumes:
    - resolution 5 10^{-5} cm^3
    - accuracy 10^{-3} cm^3
  - Temperature: ± 1°C
  - Pressure:
    - HP: ±1 bar
    - BP: ±10^{-3} bar
  - Viscosity: ±10^{-2} cPo

PVT modeling

Summary

PVT modeling



3. Thermodynamic model

Summary

Liquid-Vapor equilibrium

Summary

- **Data:**

$$Z_i = X_i \cdot L + Y_i \cdot V$$ **Balance by component**

$$L + V = 1$$ **Global balance**

$$K_i = Y_i / X_i$$ **Equilibrium constant**

$$\sum X_i = \sum Y_i = 1$$ **Balance by phase**

- **Calculations:**

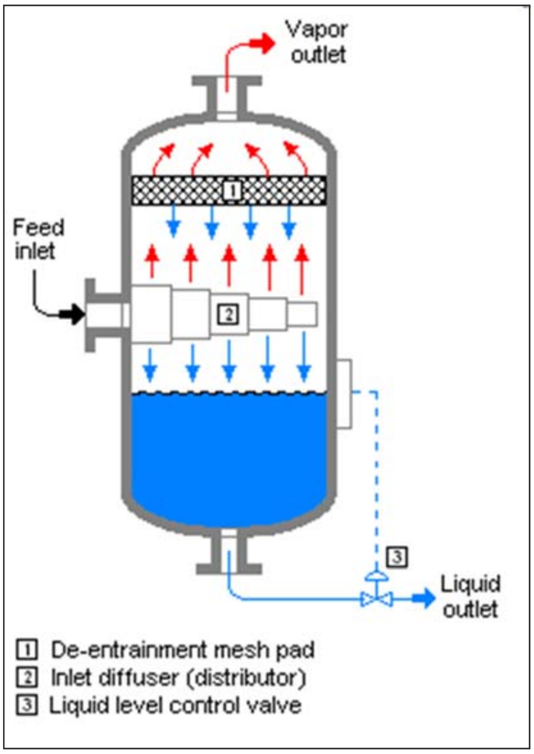
$$Z_i = X_i \cdot (1 - V) + K_i \cdot X_i V$$
$$\text{so}: \; X_i = Z_i \Big/ \left[1 + V\left(K_i - 1\right)\right]$$
$$Y_i = K_i \cdot Z_i \Big/ \left[1 + V\left(K_i - 1\right)\right]$$

- **Rachford-Rice equation:**

$$f(V) = \sum Z_i (K_i - 1) / [1 + V(K_i - 1)] = 0$$

resolution by Newton's method

$$V^{(n+1)} = V^{(n)} - \left[f\left(V^{(n)}\right) / f'\left(V^{(n)}\right)\right]$$



Flash

$$\sum_{i=1}^{n} \frac{Z_i\left(K_i - 1\right)}{1 + V\left(K_i - 1\right)} = 0$$

Bubble point

$$\sum_{i=1}^{n} K_i Z_i = 1$$

Dew point

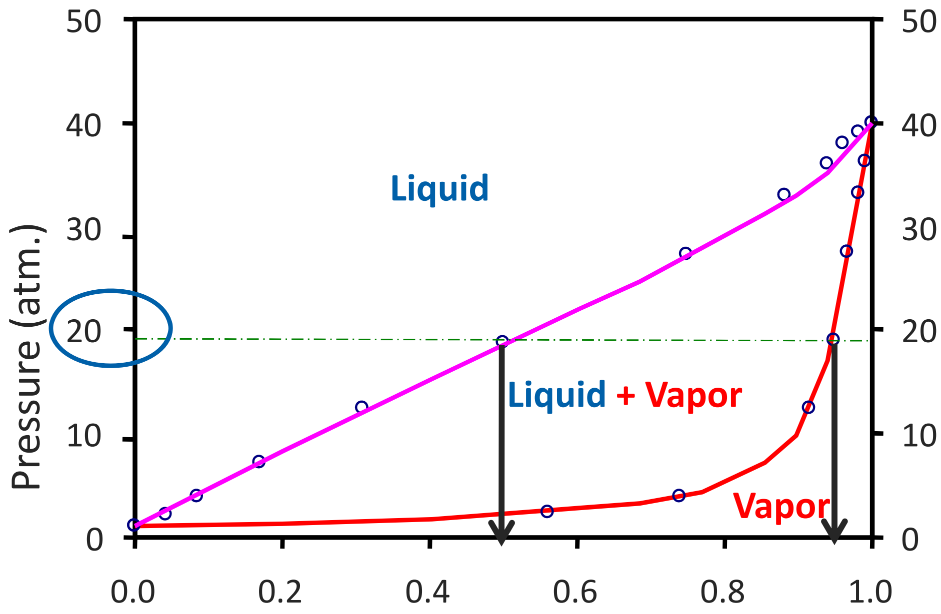
$$\sum_{i=1}^{n} \frac{Z_i}{K_i} = 1$$

Cal calculation of K values

$$K_i = \frac{y_i}{x_i}$$

- **Experiments:**
  - Binary or ternary diagrams,
  - Detailed analysis.
- **Iterative calculations:**
  - Estimated initial values.

Liquid-vapor equilibrium diagram
Methane - Ethane (-87.06°C)

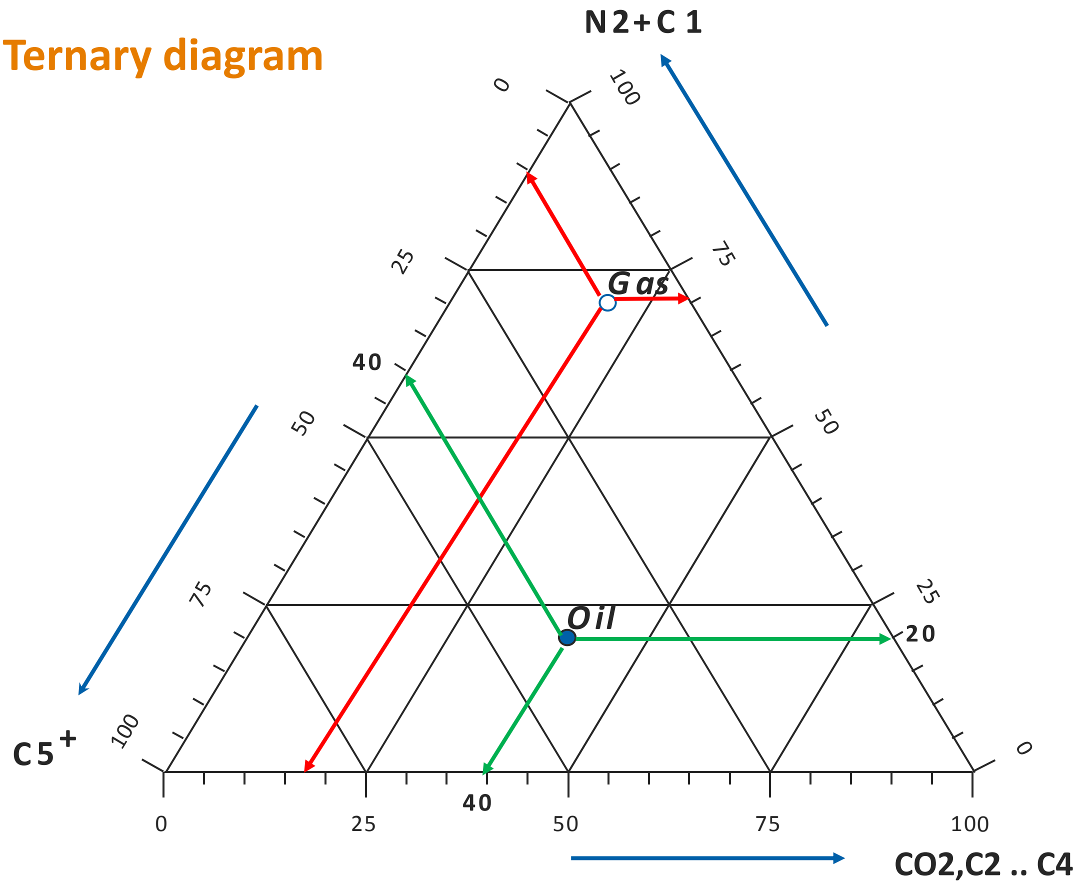


X1=0.5, Y1=0.95

X2=0.5, Y2=0.05

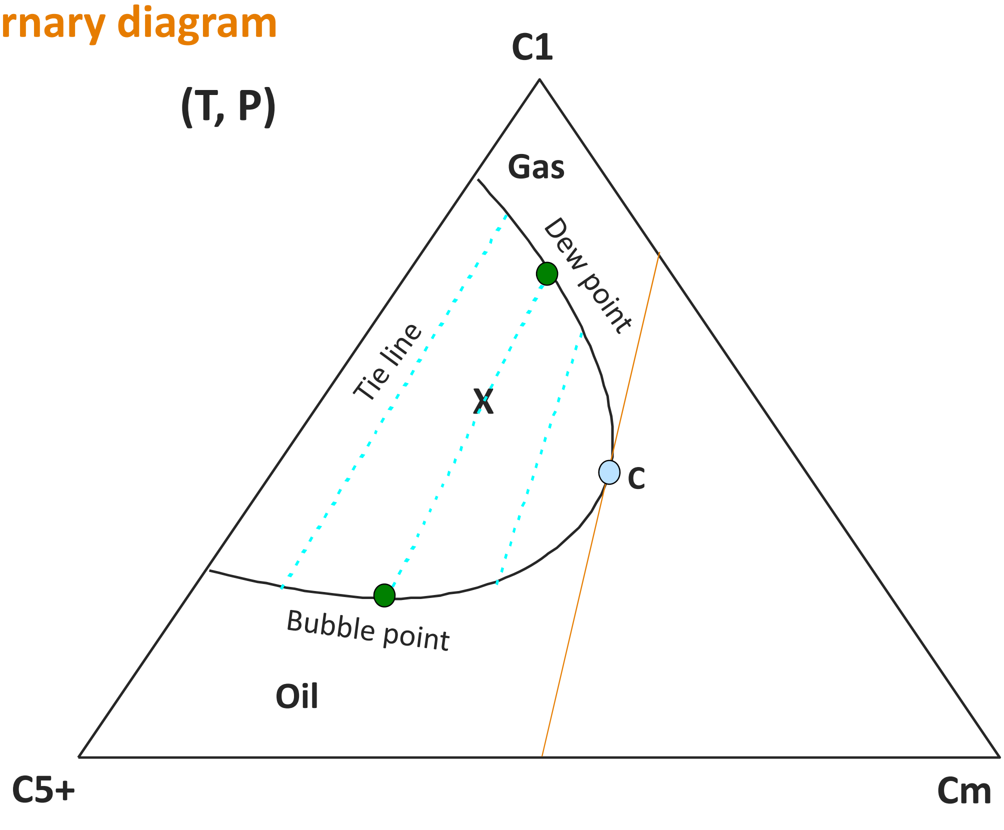
K1=1.9, K2=0.10

Ternary diagram

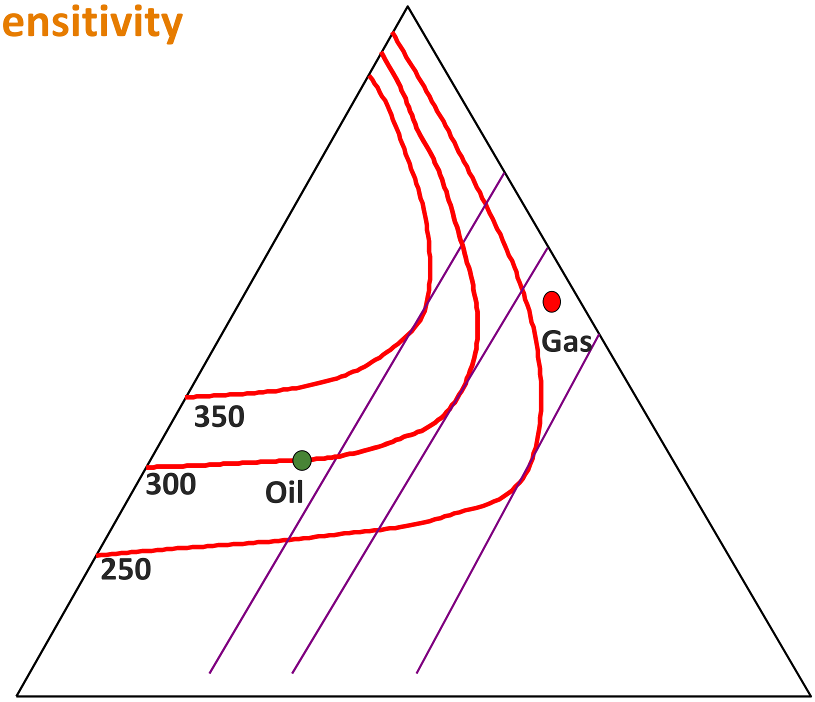


Ternary diagram

(T, P)



Ternary diagram: pressure sensitivity



Initial value for Ki

WILSON's correlation

$$C_0 = \frac{7}{3}\ln(10)$$

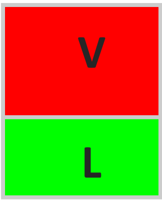
$$k_i = \exp\left\{C_0 \cdot (1 + w_i) \cdot \left(1 - \frac{T_{C_i}}{T}\right)\right\} \cdot \frac{P_{C_i}}{P}$$

WHITSON's correlation

$$C_1 = \frac{69 \cdot M_n - 4200}{14.696} C_2 = 1 - \left(\frac{P - 1}{C_1 - 1}\right)^{0.6}$$

$$k_i = \left(\frac{P_{C_i}}{C_1}\right)^{C_2 - 1} \cdot \exp\left\{C_0 \cdot C_2 \cdot (1 + w_i) \cdot \left(1 - \frac{T_{C_i}}{T}\right)\right\} \cdot \frac{P_{C_i}}{P}$$

- **State functions**
- **Free enthalpy G (Gibbs)**
  - G = H - T.S = (U + PV) - TS
  - dG = - S.dT + V.dP
- **At the equilibrium some of these functions display a minimum. In particular: dG = 0 (T, P system)**



$$\left.\begin{matrix} G_V, & g_i^V, & n_i^V \\ G_L, & g_i^L, & n_i^L \end{matrix}\right\} \quad n_i^V + n_i^L = n_i$$

Equilibrium: $g^V_i = g^L_i$

$$g_i = g_i^o + RT\ln\left(\frac{f_i}{f_i^o}\right)$$

f_i : fugacity

Liquid – Vapour equilibrium

$f_i^V = f_i^L$ for all "i"

Liquid — Vapor equilibrium

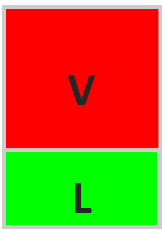
- **State variables**
  - Temperature, Pressure, Volume, ...
- **State functions**
  - Internal energy U
    - dU = dQ + dW
  - For a reversible transformation:
    - dQ = T.dS (S: entropy)
  - Enthalpy H
    - H = U + P.V
    - dH = T.dS + V.dP
  - Free energy A (Helmholtz)
    - A = U - T.S
    - dA = - S.dT - P.dV
  - Free enthalpy G (Gibbs)
    - G = H - T.S
    - dG = - S.dT + V.dP

- **Thermodynamics potentials**
  - At equilibrium, some of these state functions display a minimum; by analogy with potential energy, these functions are called

THERMODYNAMICS POTENTIALS

- **In particular:**
  - dG = 0 (T, P system)
  - dA = 0 (T, V system)

Liquid — Vapor equilibrium



$$\left.\begin{array}{l} G_V,\ g_i^V,\ n_i^V \\ G_L,\ g_i^L,\ n_i^L \end{array}\right\} n_i^V + n_i^L = n_i$$

Disturbance and return to equilibrium such that:

$$dG = dG_V + dG_L = 0$$

i.e. $\sum_i g_i^V dn_i^V = -\sum_i g_i^L dn_i^L$ with $dn_i^V = -dn_i^L$

$$\sum_i \left(g_i^V - g_i^L\right) dn_i = 0 \quad \forall i$$

$$\boxed{g_i^V = g_i^L \quad \forall i}$$

Chemical potential gi and fugacity fi

$$g_i = g_i^o + RT \ln\left(\frac{f_i}{f_i^o}\right)$$

Liquid - Vapor Equilibrium

$$f_i^v = f_i^L \quad \text{for all "i"}$$

Reference: Ideal gas at T and P

$$f_i^o = x_i P$$

Coefficient of fugacity

$$\varphi_i = \frac{f_i}{x_i P}$$

At equilibrium

$$K_i = \frac{y_i}{x_i} = \frac{\varphi_i^L}{\varphi_i^V}$$

Equation of state (EOS)

Summary

Equations of state

MARIOTTE 1650	$P = \frac{RT}{V}$
VAN DER WAALS 1873	$P = \frac{RT}{V-b} - \frac{a_c}{V^2}$
CLAUSIUS 1880	$P = \frac{RT}{V-b} - \frac{a_c}{T(V+c)^2}$
BERTHELOT	$P = \frac{RT}{V-b} - \frac{a_c}{TV^2}$
REDLICH KWONG	$P = \frac{RT}{V-b} - \frac{a_c T^{-0.5}}{V(V+b)}$
WILSON 1964	$P = \frac{RT}{V-b} - \frac{A(T)}{V(V+b)}$
SOAVE REDLICH KWONG 1972	$P = \frac{RT}{V-b} - \frac{B(T)}{V(V+b)}$
PENG - ROBINSON 1976	$P = \frac{RT}{V-b} - \frac{C(T)}{V(V+b)+b(V-b)}$
PATEL TEJA 1981	$P = \frac{RT}{V-b} - \frac{D(T)}{V(V+b)+c(V-b)}$

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

$$a(T) = a(T_c)\,f(T)$$

$$a(T_c) = \Omega_a \frac{R^2T_c^2}{P_c}$$

$$\Omega_a = 0.4572$$

$$b = b(T_c)$$

$$b(T_c) = \Omega_b \frac{RT_c}{P_c}$$

$$\Omega_b = 0.0778$$

Peng – Robinson's Equation

$$f(T) = \left[1 + m\left(1 - \sqrt{T_r}\right)\right]^2$$

$\omega < 0.49$ (nC_{10})

$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$

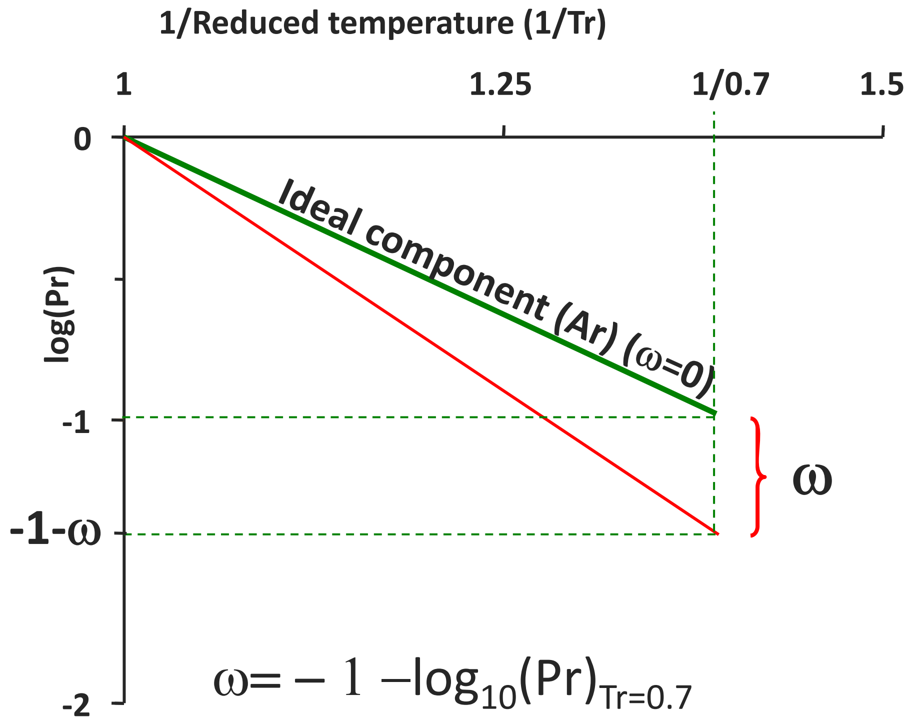
$\omega > 0.49$

$m = 0.379642 + 1.48503\,\omega - 0.164423\,\omega^2 + 0.016666\,\omega^3$

$$Z = \frac{PV}{RT} \qquad A = \frac{aP}{R^2T^2} \qquad B = \frac{bP}{RT}$$

$$Z^3 + (B-1)Z^2 + (A - 3B^2 - 2B)Z + (B^3 + B^2 - AB) = 0$$

Acentric factor w



$$\omega = -1 - \log_{10}(Pr)_{Tr=0.7}$$

(Pitzer's factor)

Fugacity

General expression for a pure component:

$$\boxed{\ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_V^{inf}\left(P - \frac{RT}{V}\right)dV + Z - \ln Z - 1}$$

Peng-Robinson's Equation:

Fugacity coefficient: $\frac{f}{P}$

$$\ln\left(\frac{f}{P}\right) = Z - 1 - \mathrm{Log}(Z - B)$$

$$- \frac{A}{2\sqrt{2}B} \cdot \ln\left(\frac{Z + 2.414 \cdot B}{Z - 0.414 \cdot B}\right)$$

Combination rules

Pure components ➔ mixture

$$P = \frac{RT}{V - b_m} - \frac{a_m(T)}{V(V + b_m) + b_m(V - b_m)}$$

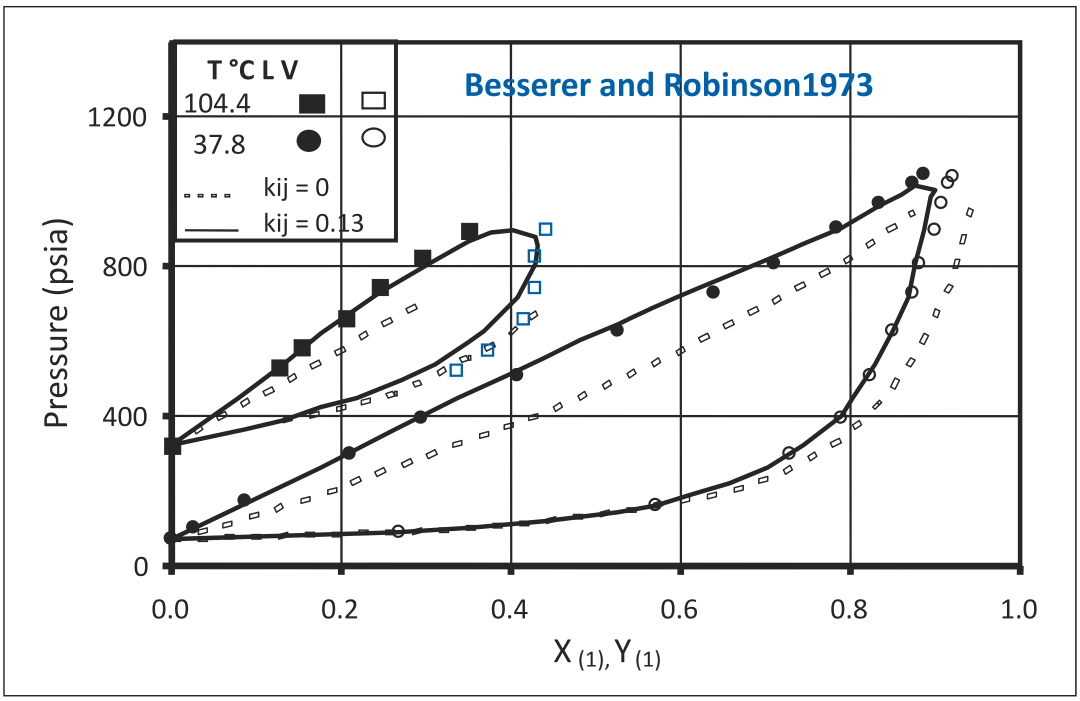
$$b_m = \sum_{i=1}^{n} x_i \cdot b_i$$

$$a_m = \sum_{j=1}^{n} \sum_{i=1}^{n} x_i \cdot x_j \cdot (1 - k_{ij}) \cdot \sqrt{a_i \cdot a_j}$$

$$k_{ij} = \text{Binary interaction coefficients}$$

Liquid — Vapor equilibrium

Binary diagram: CO2-iC4 (experiment and EOS calculations)

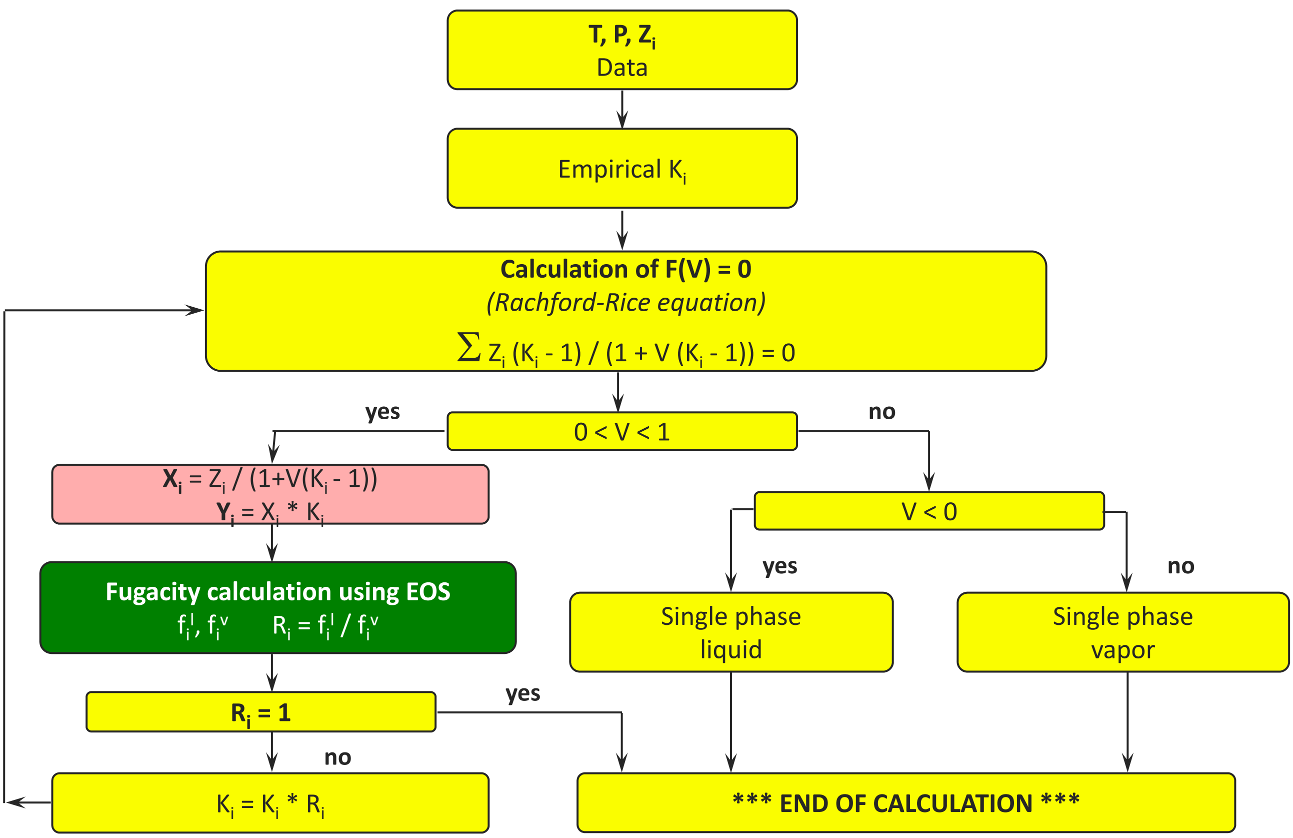


Fugacity coefficient of component k in a mixture

Peng-Robinson's Equation:

$$\mathrm{Log}\left(\frac{f_k}{Px_k}\right) = \frac{b_k}{b_m}(Z-1) - \mathrm{Log}(Z-B)$$
$$-\frac{A}{2\sqrt{2}B}\left(\frac{2\sum_i^n x_i a_{ik}}{a_m} - \frac{b_k}{b_m}\right)$$
$$\times \mathrm{Log}\left(\frac{Z+2.414B}{Z-0.414B}\right)$$

$$\text{with: } a_{ik} = (1-k_{ik})\cdot\sqrt{a_i \cdot a_k}$$



Liquid — vapor equilibrium

Generalized NEWTON's method

- **Target function** $F_i = f_i^L - f_i^V \quad (n\,\text{component vector})$
  - n variables
  - $X_1, X_2, \ldots, X_{n-1}$ and L → R (vector of iteration variables)

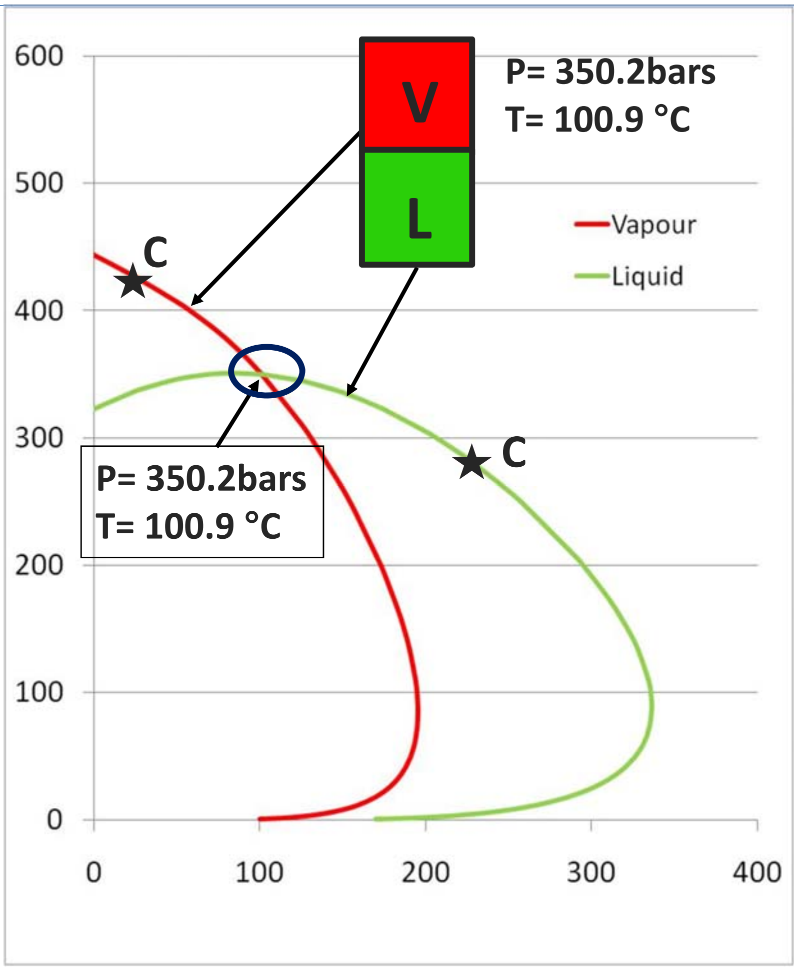
- **Newton's method:** $J^\lambda (R^{\lambda+1} - R^\lambda) = F^\lambda$
  $(J : F(R)\ \text{jacobian})$
  $j_{i1} = \partial F_i / \partial L \quad i \in [1, nc]$
  $j_{ik} = \partial F_i / \partial x_k \quad i \in [1, nc]$
  $k \in [1, nc-1]$

- **For the next iteration, the solution vector R is given by:**

$$R^{\lambda+1} = R^\lambda - \left[J^\lambda\right]^{-1} F^\lambda$$

(quadratic convergence)

Liquid — vapor equilibrium and phase envelopes



Compositional grading

Summary

Standard compositional grading with depth

Variation of composition with depth

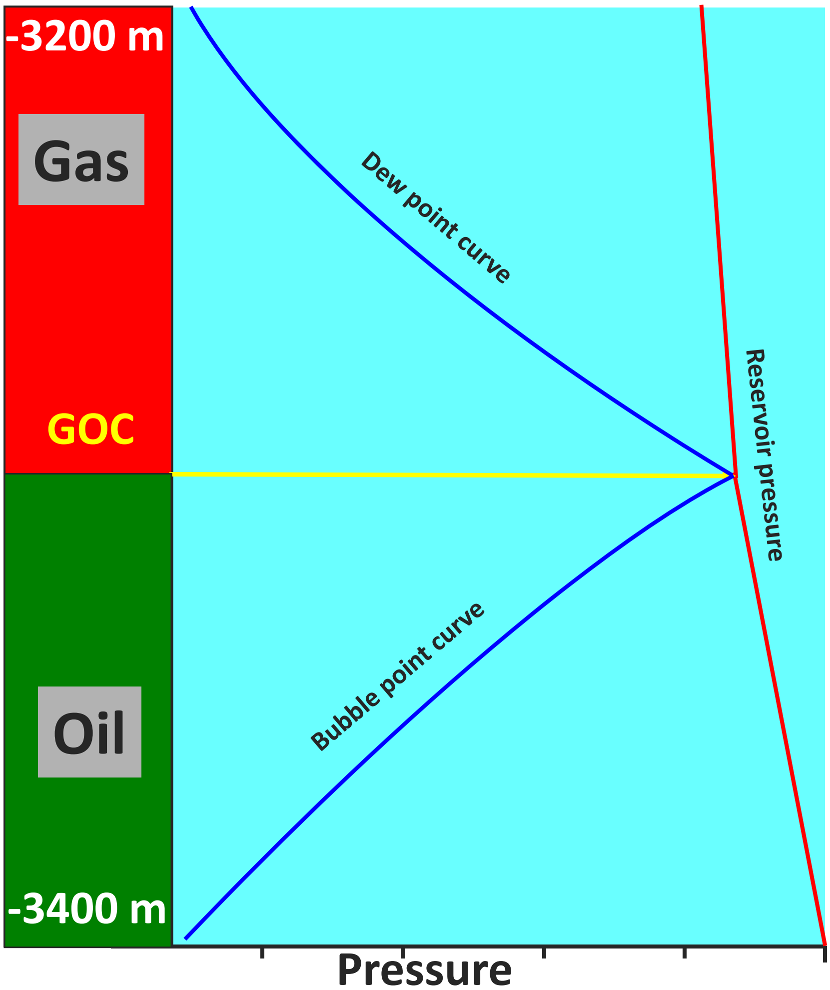
- **Knowing the composition, and pressure p° at the reference height h°**
- **Calculate the composition and pressure at other heights**
- **Ignoring the compositional gradient in petroleum reservoirs may result in bad reservoir management**

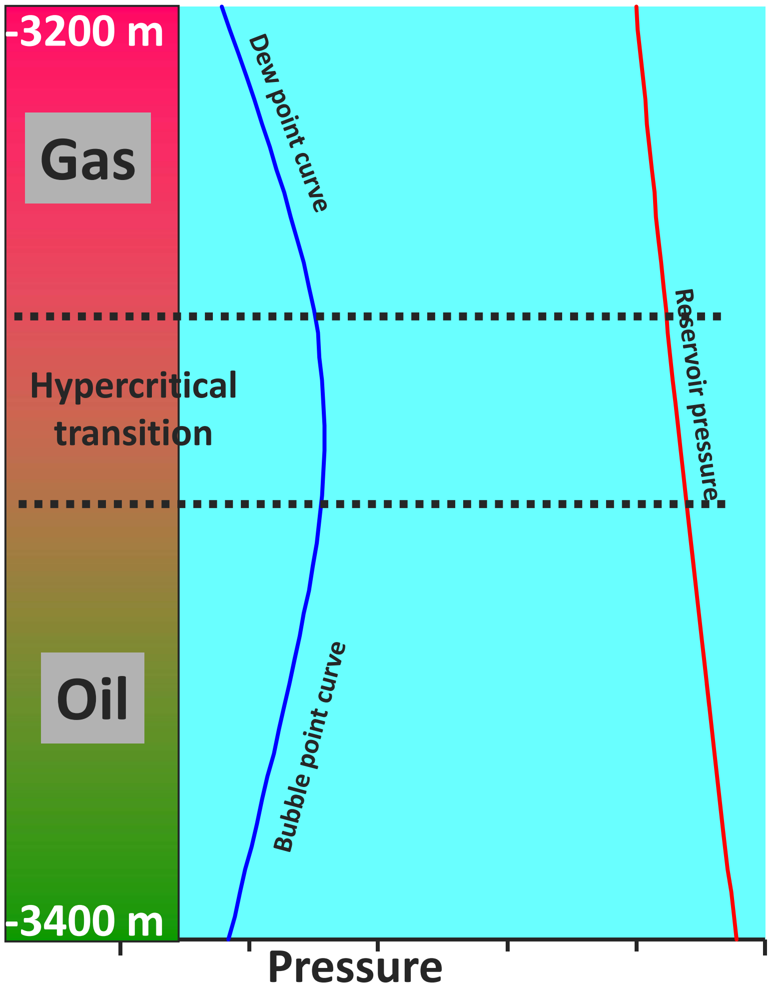
Standard compositional grading with depth

Variation of composition with depth

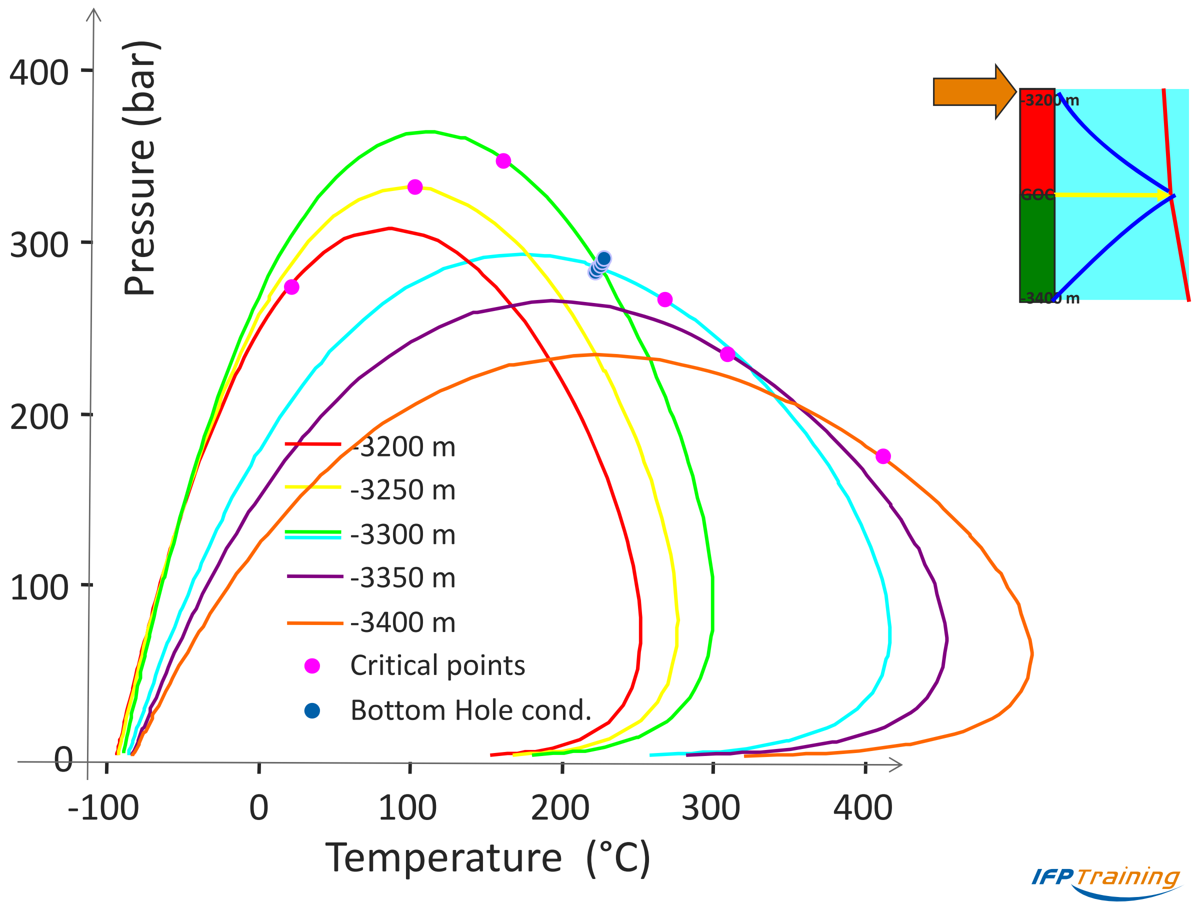
- As hydrocarbons move into the reservoir rocks from source, they are influenced by the Earth's gravity, the temperature field, and capillary forces.
- Gravity forces tend to segregate the heavier and lighter components.
- Thus, lighter components move upwards while heavier components move downwards.
- Temperature acts in an opposite direction and reduces the intensity of the movements.
- The resulting effect is the decrease in solution gas oil ratio, formation volume factor of oil and bubble point pressure, and an increase in the viscosity and gasdew pressure with depth

Standard compositional grading with depth



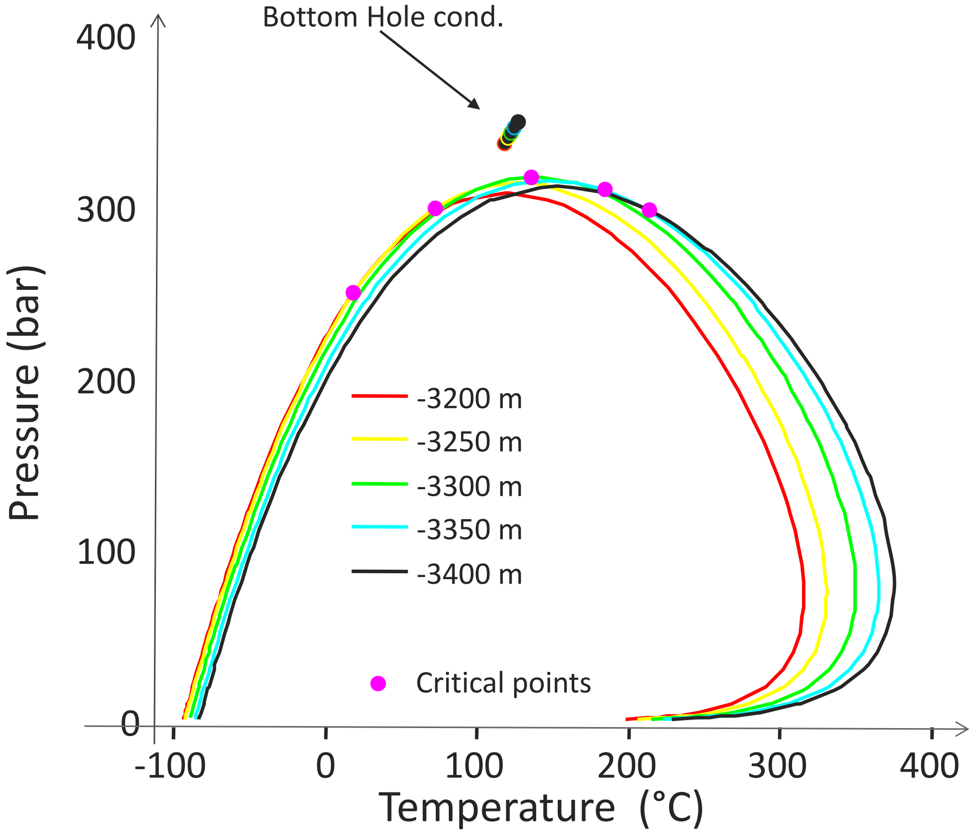


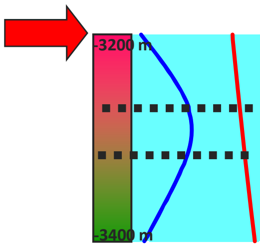
GOC transition: evolution of the phase envelopes



Compositional grading with depth

Hypercritical transition: evolution of the phase envelopes

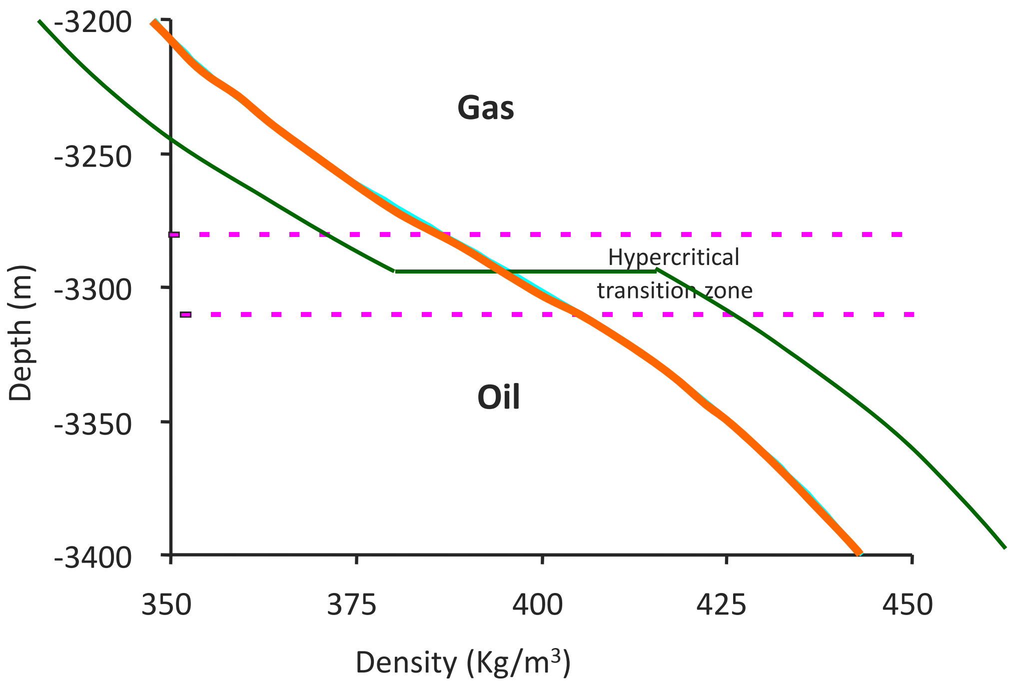




There is no point where the bottom hole conditions are on the phase envelope, the fluid is never saturated and there is no GOC

Compositional grading with depth

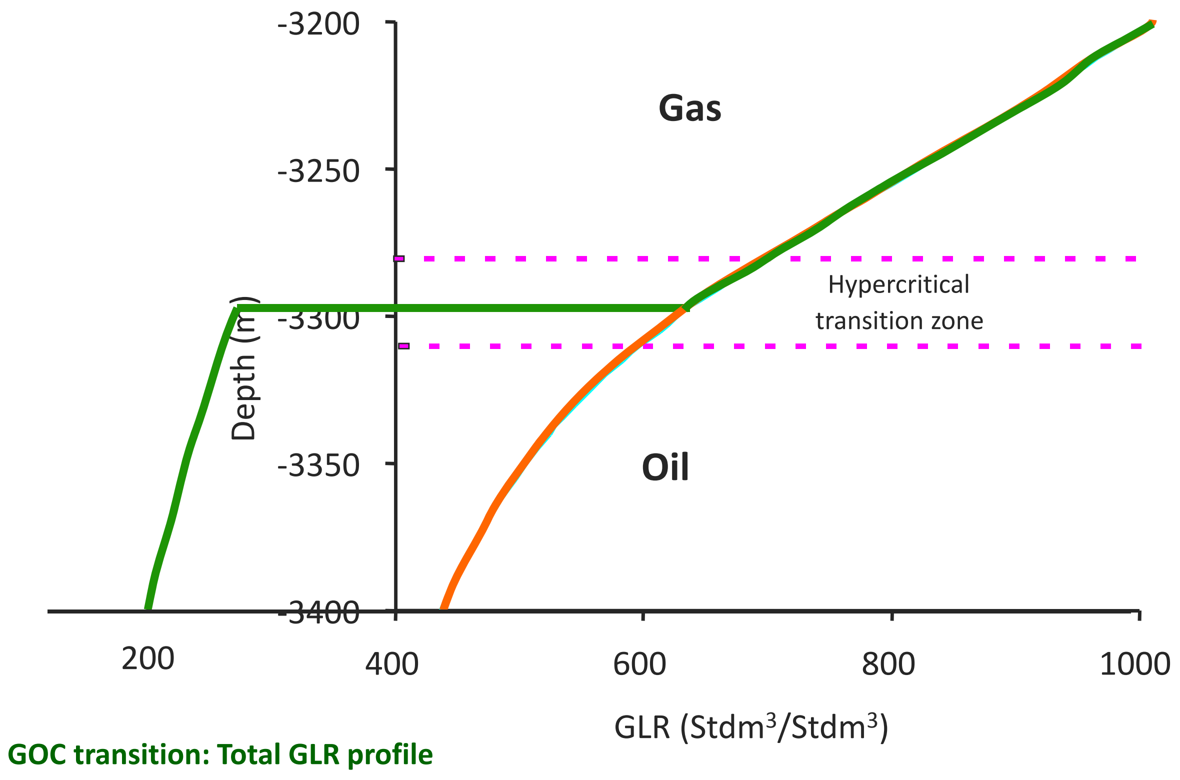
Hypercritical transition: BH density profile



GOC transition: BH density profile

Compositional grading with depth

Hypercritical transition: Total GLR profile



Compositional grading with depth

- Due to the gravity (γ) effect, the chemical potential "g_i" varies with depth:

$$d\, g_i = m_i\, \gamma\, dh$$

- We know that:

$$g_i = g_i^0 + RT \,\mathrm{Ln}\,(f_i / f_i^0)$$

$$\rightarrow d\, g_i = RT\, d\,(\mathrm{Ln}\, f_i)$$

$$(m_i\, \gamma / RT)\, dh = d\,(\mathrm{Ln}\, f_i)$$

$$\text{so: } m_i\, \gamma h / RT - 0 = \mathrm{Ln}\, f_i^h - \mathrm{Ln}\, f_i$$

$$\boxed{f_i^h / f_i = \exp\,(m_i\, \gamma h / RT)}$$

Compositional grading with depth

Algorithm

Data @ depth H: ***P, T, Zi***
fugacity ***fi***
Ri *initialisation*

New depth ***H'=H+h***
New pressure $P'_f = P_f + \rho\gamma h$

Zi'= Ri*Zi: new fugacity f'_i

$$R_i = R_i^{old}\left(\frac{f_i}{f'_i}\right)\cdot\exp\left(\frac{m_i\gamma h}{RT}\right)$$

Convergence test $\left|\frac{R_i}{R_i^{old}} - 1\right| < 10^{-7}$

New temperature : $T' = T + h\,\frac{dT}{dH}$

Saturation pressure @ T': P_s

Test for GOC location
$P_s < P_f$

Yes

Interface

No

Matching of experimental data

Summary

Matching Methodology

Methodology

- As few EOS parameters as possible
- Most poorly defined components (highest uncertainty)
- Maintain properties monoticity
- Change properties by a few percent, if possible
- Weight important measurements
- Require “match” to reservoir and surface conditions
- Swelling test for injection schemes?

Trial and error until acquire “engineering feel”

Matching Methodology

Prior to matching

- **Check measured data for consistency and quality**
  - Compositions sum to 100%?
  - Pressure-dependent data: correct trends?
  - Material balance on CVD?
  - Property definitions?
  - Consistent units?
  - Plus fraction description?
- **EOS: Use three-parameter model - extra degree of freedom in c_i (Volume Shift)**

Matching methodology

- **Choice of the variables**
  - T_c, p_c, ω of Cn+ fraction(s): saturation pressure, liquid dropout, etc.
  - Volume shift: Z-factors, densities, etc.
  - Z_c or V_c for LBC viscosity
  - Parachor for interfacial tension
- **Dangers**
  - The "traditional" matching procedure is to adjust $k_{C1,Cn+}$ to obtain measured p_{sat}
  - May imply a phase diagram deviation at low temperature.
  - Engineer must decide if deviation will affect the simulation results or separator flashes

Matching methodology

Dangers

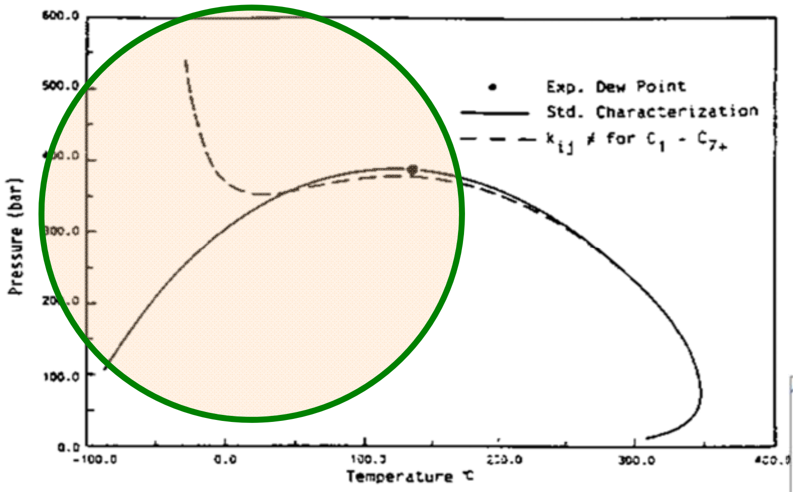
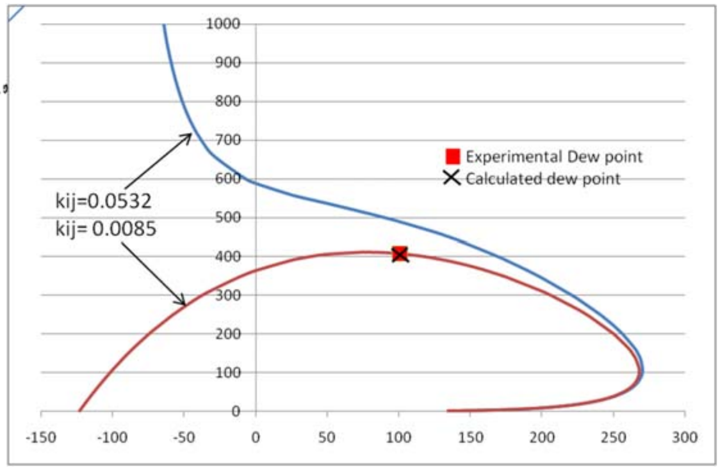
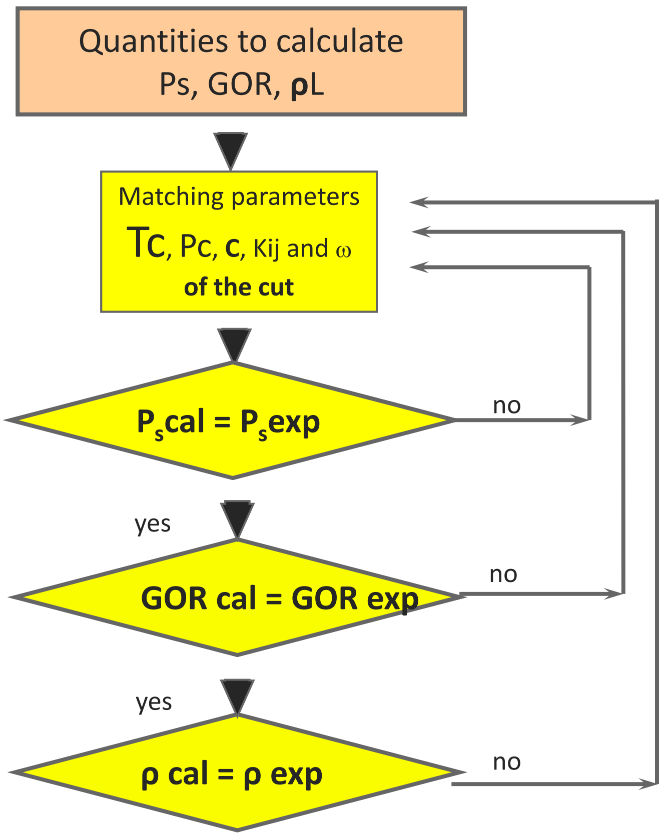


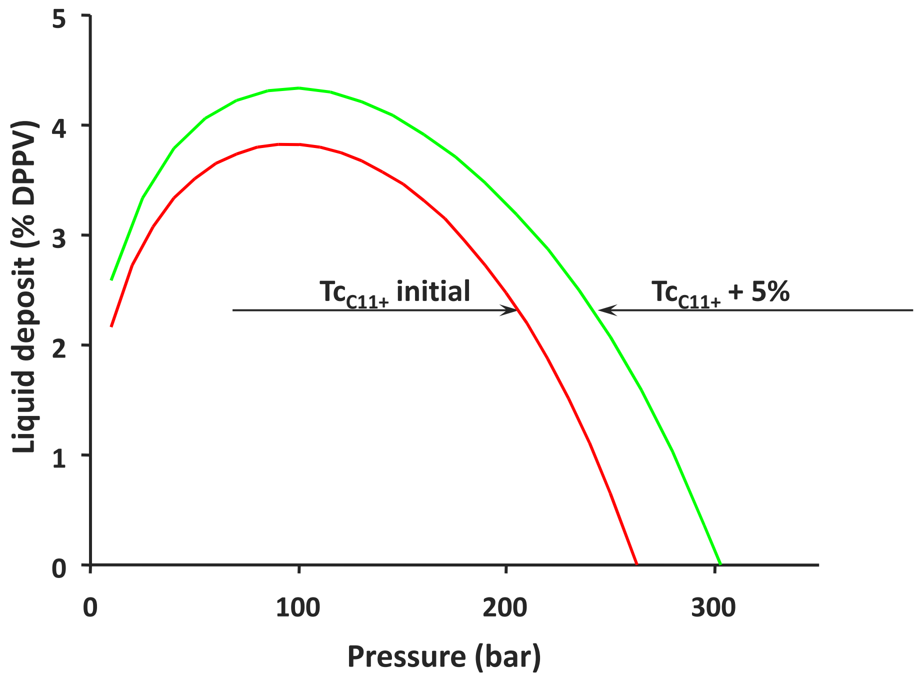
Figure 10-4. Phase envelope calculated for the gas condensate mixture for which the molar composition is given in Table 10-1. ,



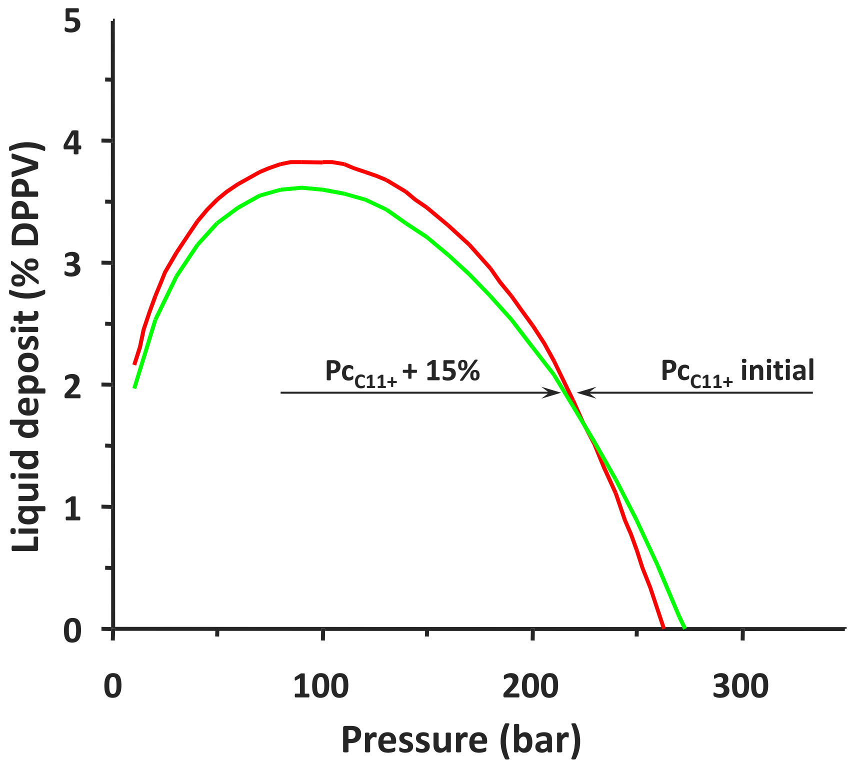
Matching algorithm



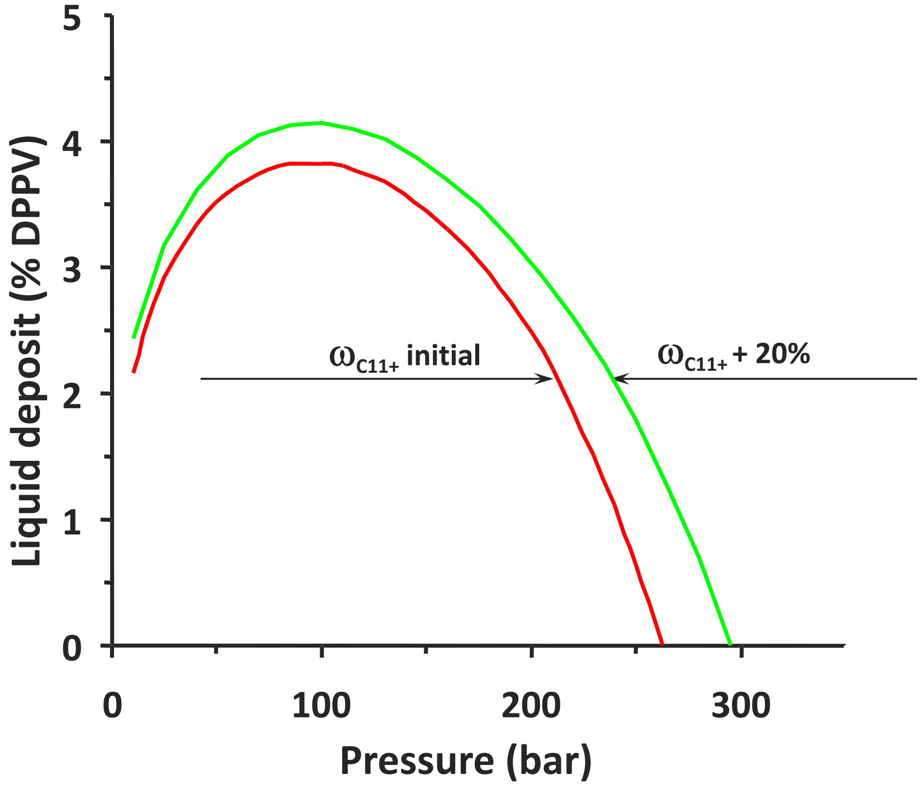
Influence of Tc on the liquid deposit



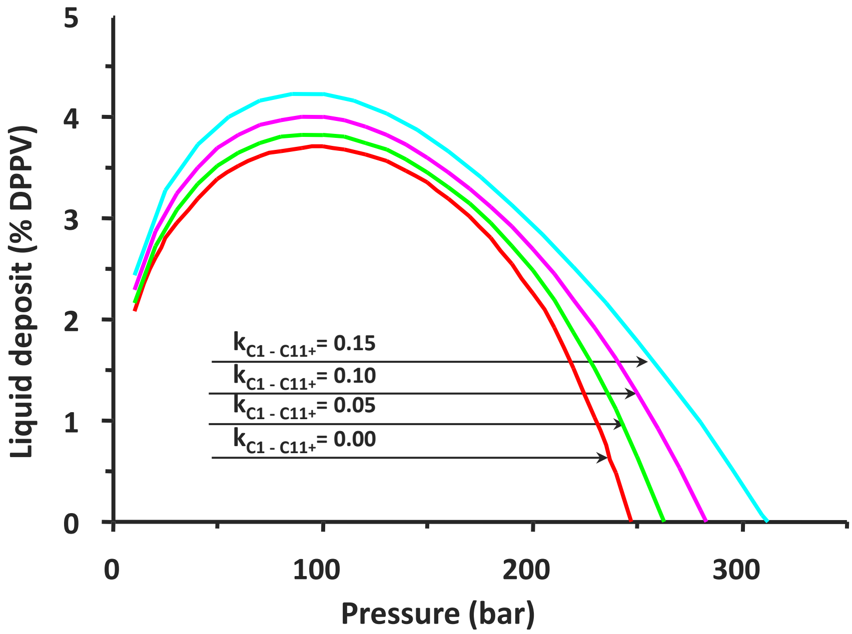
Influence of Pc on the liquid deposit



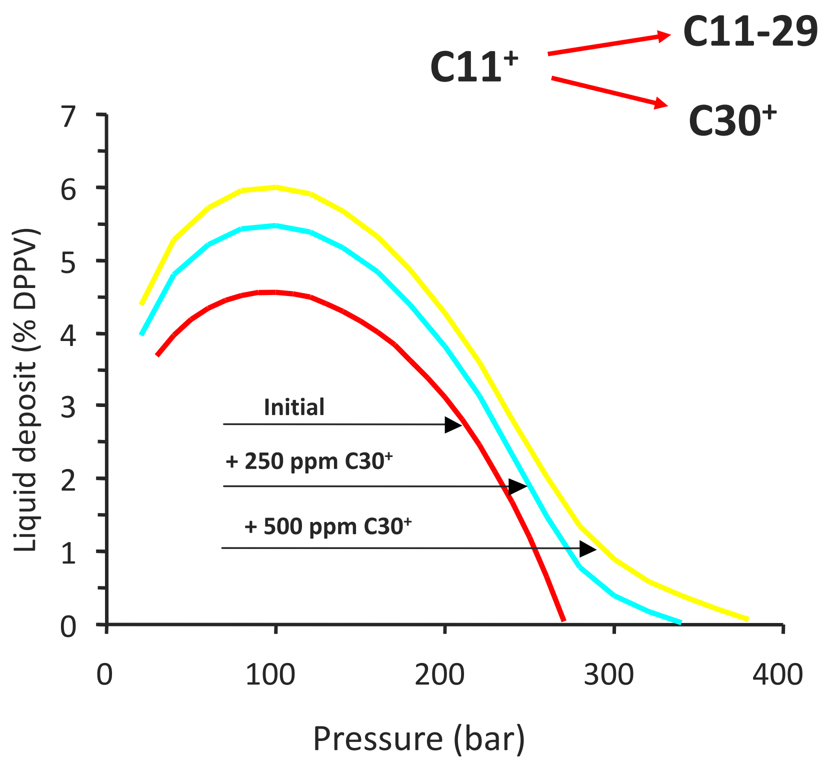
Influence of ω on the liquid deposit



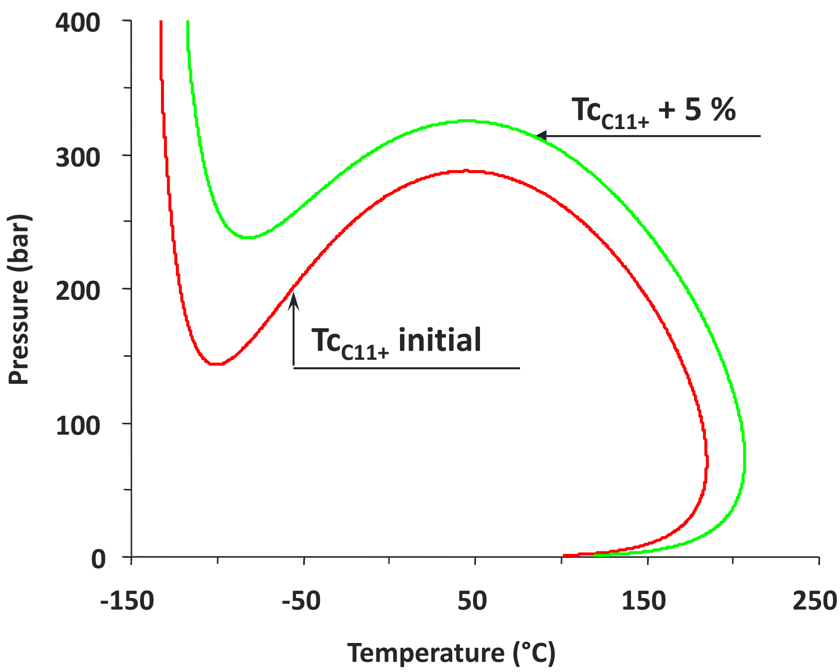
Influence of Kij on the liquid deposit



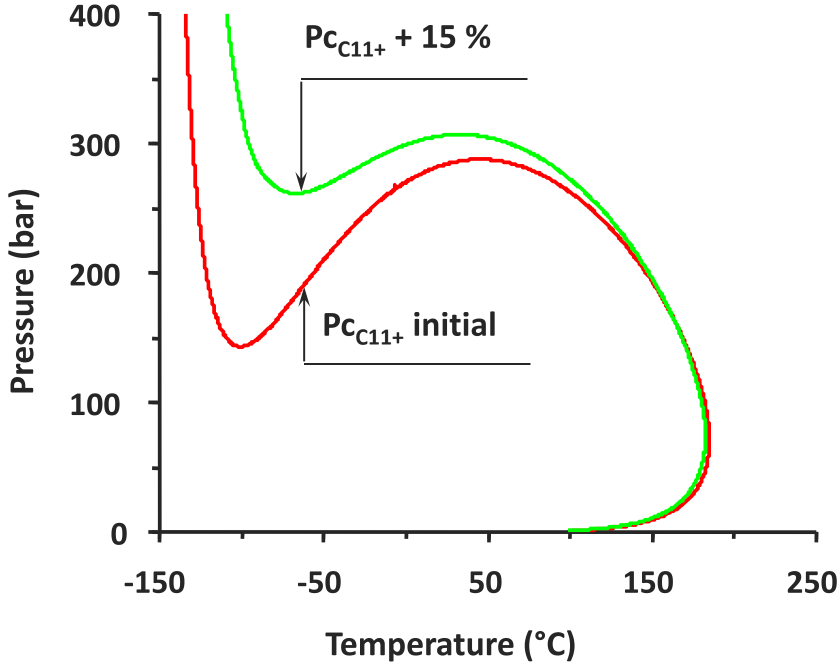
The “split” of the heavy cut



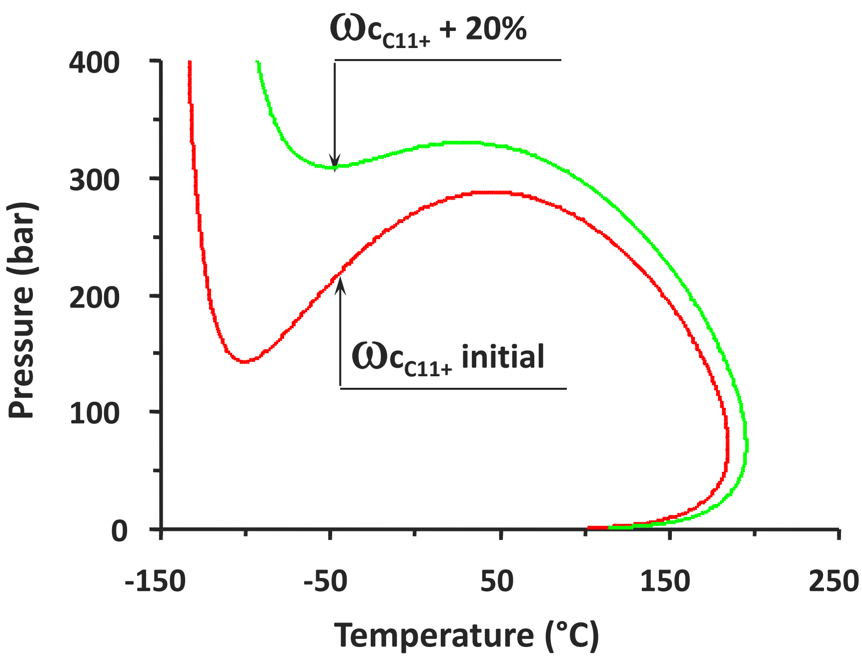
Influence of Tc on the envelope



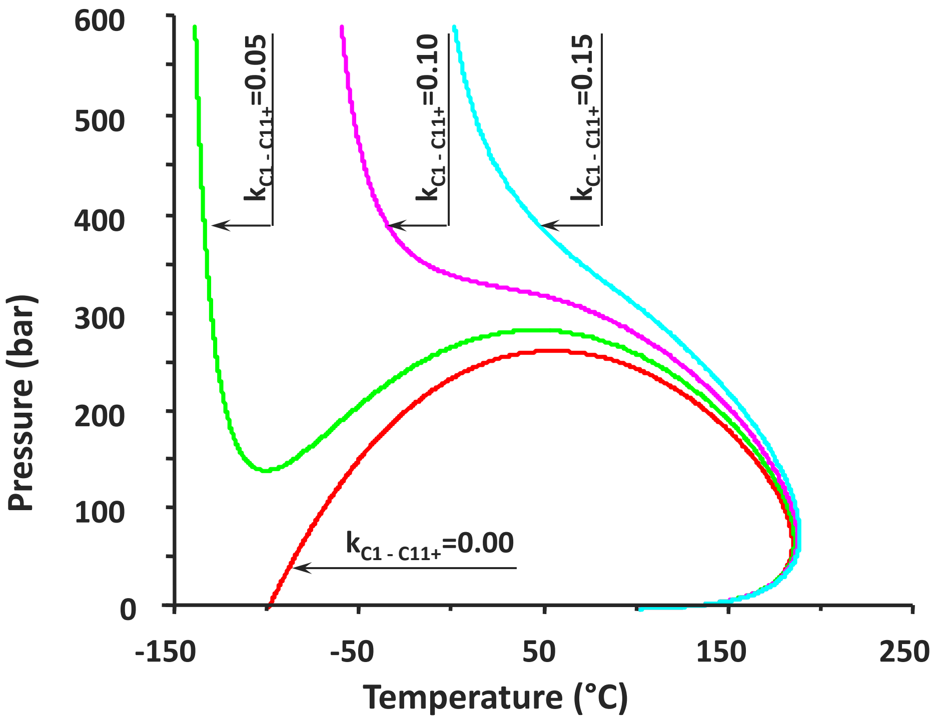
Influence of Pc on the envelope



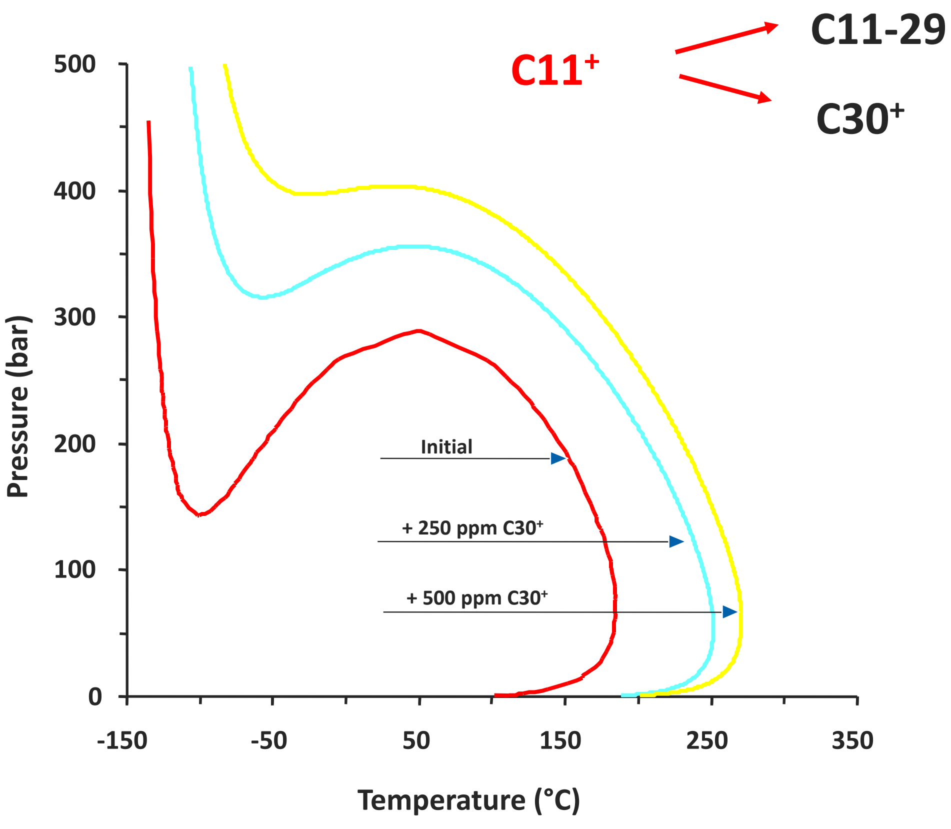
Influence of ω on the envelope



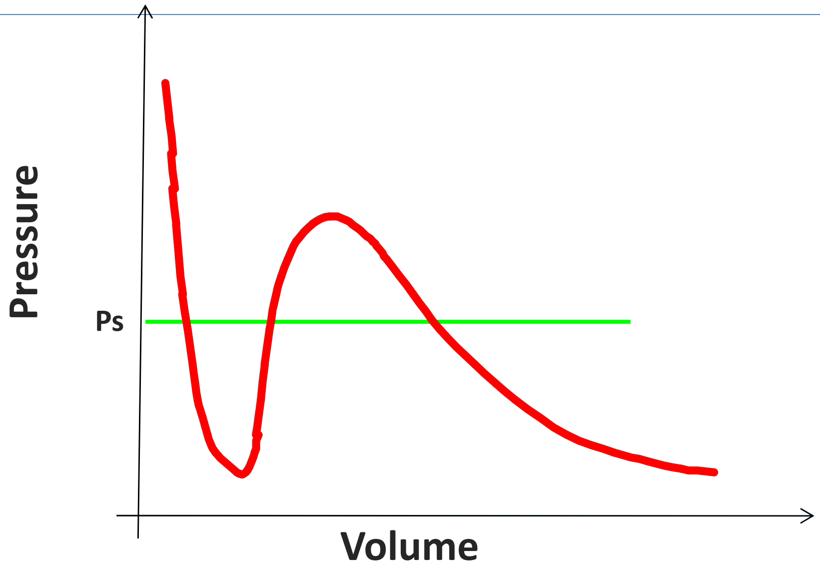
Influence of Kij on the envelope



The "split" of the heavy cut



Volume shift



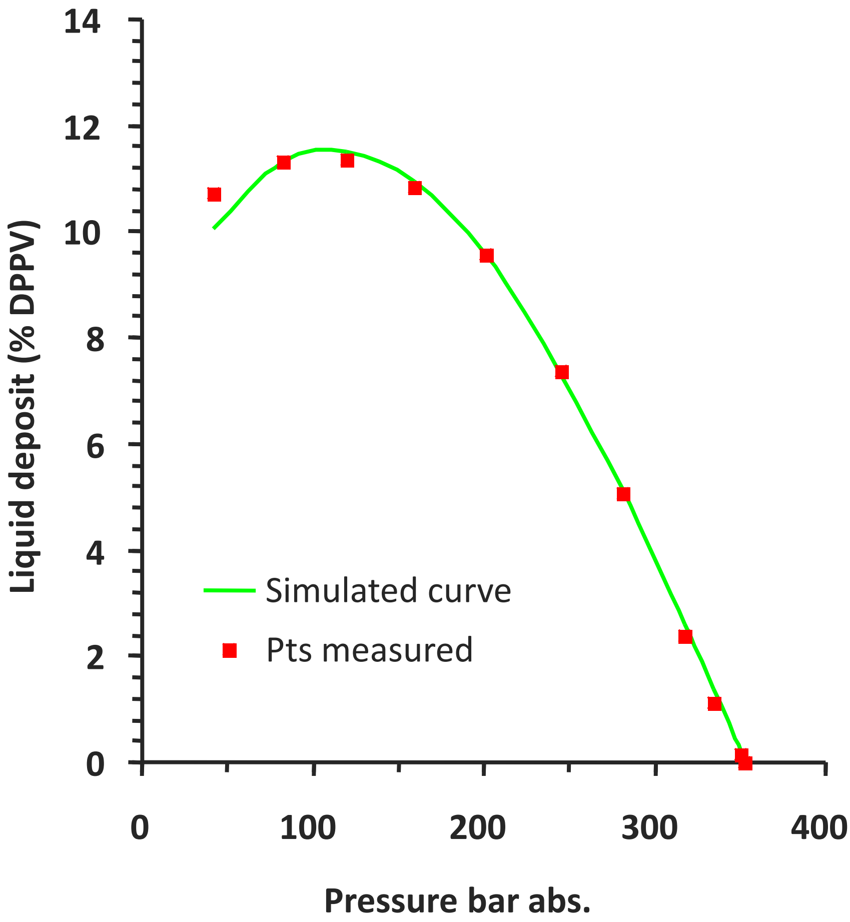
$$V = V^{EOS}$$

➔ **Matching of both bottom hole and surface densities**

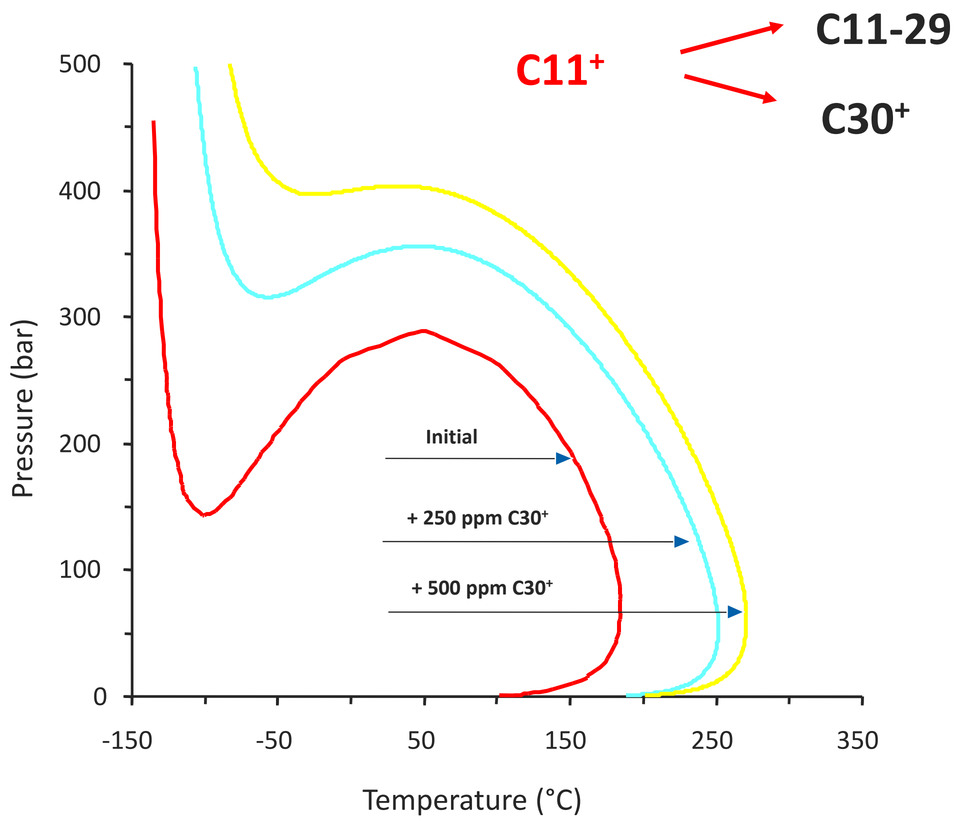
Results of a 14-component match

	Measured values	Simulated values	Relative error %
$P_{rosée}$	353.000	353.000	0.00
ρ_V à P_{sat}	0.315	0.315	0.00
ρ_V à P_{fond}	0.312	0.313	0.32
GOR sep	1631.800	1733.542	6.24
ρ_L sep	0.722	0.730	1.11
GOR total	2055.770	2071.080	0.74
ρ_L Std	0.779	0.767	1.54
Simulation of liquid deposit			
Pressure bar abs	Measured values	Simulated values	
353.0	0.000	0.000	
350.0	0.135	0.230	See figure
334.5	1.111	1.396	
318.0	2.368	2.596	
281.0	5.075	5.128	
245.5	7.359	7.314	
201.0	9.574	9.558	
159.0	10.824	10.952	
120.0	11.360	11.500	
82.0	11.313	11.303	
42.0	10.722	10.066	

Results of a 14-component match



The "split" of the heavy cut



Splitting

- "Insufficient description of heavier hydrocarbons reduces the accuracy of PVT predictions" Whitson C.H., SPEJ, p. 683, Aug. 1983
- Condensates and Volatile Oils are particularly sensitive to the composition and properties of the plus fraction
- Laboratories tend to give very limited analysis to the plus fraction, i.e., M_{N+}, γ_{N+}
- Requires an automatic procedure to characterize the plus fraction
- Whitson (1980)
- Pedersen et al (1982)
- Katz (1983)
- Pedersen et al (1985)
- Whitson et al (1986 & 1989)

Analytical Splitting

- In splitting the heavy ends using analytical techniques, important requirements must be fulfilled:

$$\sum_{i=n}^{N+} Ci = C_n^+ \qquad \sum_{i=n}^{N+} Ci\,Mw_i = C_7^+\,Mw_7$$

- The sum of product off the mole fractions and molecular weight divided by the specific gravity of each individual component is equal to that of Cn+

$$\sum_{i=n}^{N+}\left[\frac{Ci\ Mw_i}{\gamma_i}\right] = \frac{Z_7^+\ Mw_7^+}{\gamma_7^+}$$

Ahmed (1989)

Whitson Analytical Splitting

- **Knowing the Molecular Weight and density (specify gravity) of the Cn+ fraction, Whitson splitting calculation uses a three-parameter probability density function.**

- **This procedure splits Cn+ fraction into many (30-40) small pseudo-components, then lumps them to the desired number.**

4. Characterization and modeling of heavy fractions

Summary

Heavy fractions

Summary

Heavy cut properties

- There are so many components in petroleum reservoirs that it **is impossible to obtain their exact composition.**
- Only pure components such as N_2, CO_2, H_2S, C_1-C_6 up to C_{45} may be identified, and the rest is lumped and called **heavy ends.**
- These heavy ends (or **plus fractions**) may comprise very large number of isomers, and can be defined by boiling point fractions only.
- These heavy constituents have considerable impact on the performance of EOS.

Heavy cut properties

- For use in EOS, the components should at least be characterized by their
  - critical pressure
  - critical temperature,
  - critical volume,
  - acentric factor,
  - molecular weight, and
  - density at standard conditions.

Heavy cut properties

CAVETT's method

- **Required data**
  - Boiling point Teb
  - API = 141.5 / SG – 131.5

	F	G
0	768.071	2.829
1	1.7134	0.94120 10^{-3}
2	-0.10834 10^{-2}	-0.30475 10^{-5}
3	-0.89213 10^{-2}	-0.20876 10^{-4}
4	0.38890 10^{-6}	0.15141 10^{-8}
5	0.53095 10^{-6}	0.11048 10^{-7}
6	0.32712 10^{-7}	-0.48270 10^{-7}
7	-----	0.13950 10^{-9}

- **Tc and Teb in Fahrenheit**

$$T_C = F_0 + F_1 T_{eb} + F_2 T_{eb}^2 + F_3 T_{eb} API + F_4 T_{eb}^3 + F_5 T_{eb}^2 API + F_6 T_{eb}^2 API^2$$

- **Pc in psia is given by:**

$$Log(Pc) = G_0 + G_1 T_{eb} + G_2 T_{eb}^2 + G_3 T_{eb} API + G_4 T_{eb}^3 + G_5 T_{eb}^2 API + G_6 T_{eb} API^2 + G_7 T_{eb}^2 API^2$$

Heavy cut properties

Lee-Kessler

$$p_c(\text{psi}) = 8.3634 - \frac{0.0566}{\gamma} - \left(0.24244 + 2.2989\gamma + \frac{0.11857}{\gamma^2}\right) x\,10^{-3} T_b + \left(1.4685 + \frac{3.648}{\gamma}\right)\frac{0.47227}{\gamma^2} x10^{-7} T_b^2 - \left(0.42019 + \frac{1.6977}{\gamma^2}\right) x10^{-10} T_b^3$$

$$T_c(R) = 341.7 + 811.0\gamma + (0.4244 + 0.1174\gamma)T_b + \frac{(0.4669 - 3.26223\gamma)x10^5}{T_b}$$

with $\gamma = SPGR$

Lee-Kessler

$$\omega = \frac{\left(-\ln\left(\frac{Pc}{14.696}\right) - 5.92714 + \frac{6.09648}{T_{b,r}} + 1.28862 \ln T_{b,r} - 0.169347 T_{b,r}^{6}\right)}{\left(15.2518 - \frac{15.6875}{T_{b,r}} - 13.4721 \ln T_{b,r} + 0.43577 T_{b,r}^{6}\right)}$$

$$(T_{b,r} < 0.8)$$

$$\omega = -7.904 + 0.1352 M_w - 0.007465 M_w^2 + 8.359 T_{b,r} + \frac{(1.408 - 0.01065 M_w)}{T_{b,r}}$$

$$(T_{b,r} > 0.8)$$

Standing (Mathews, Roland, Katz Correlation)

***Pc* = 1188.0 - 431.0 . *log(MW-* 61.1)**
+ (2319.0 - 852.0 . *logMW* - 53.7) . (ρ - 0.8)

Tc = 608.0 + 364.0 . dlog 10(MW - 71.2)
+ (2450.0 . *log(MW)* - 3800.0) . dlog 10(ρ)

BPR = BP + 459.67
ω = 3.0 . (log((Pc) - 2.0057)
/(7.0 . T_c/BPR - 1.0)) - 1.0

Heavy cut properties

RIAZI and DAUBERT's method

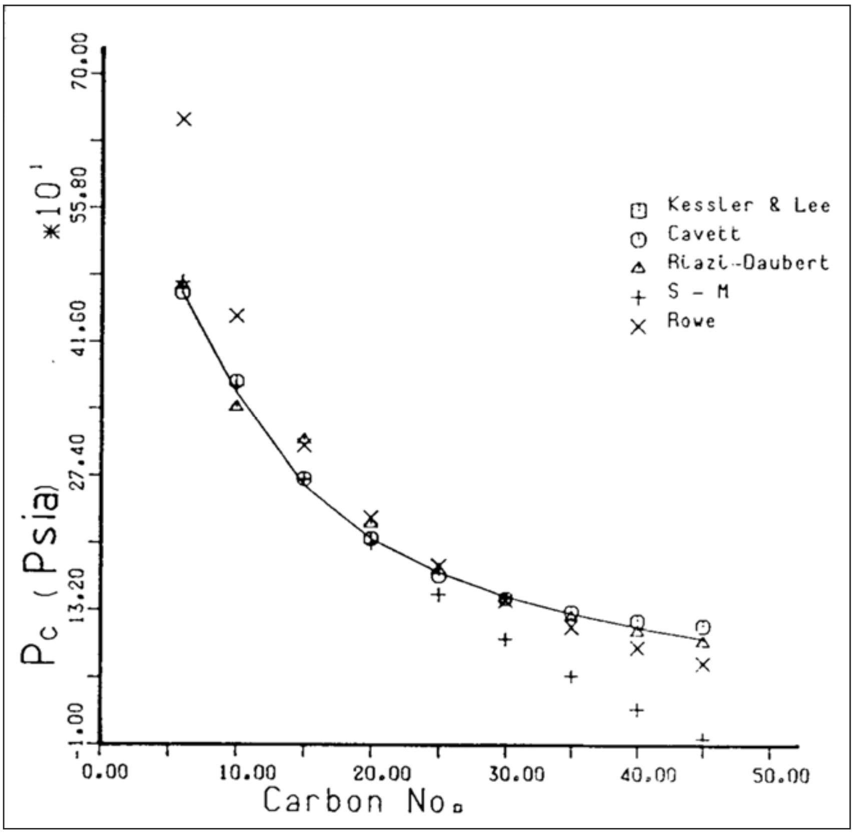
- **Required data**
  - Boiling point (Teb)
  - Specific gravity
- **Teb in Rankine**

$$\theta = aT_{eb}^{b}d^{c} \qquad \omega = \frac{3}{7}\left(\frac{\log_{10}P_c}{\frac{T_c}{T_{eb}} - 1}\right) - 1$$

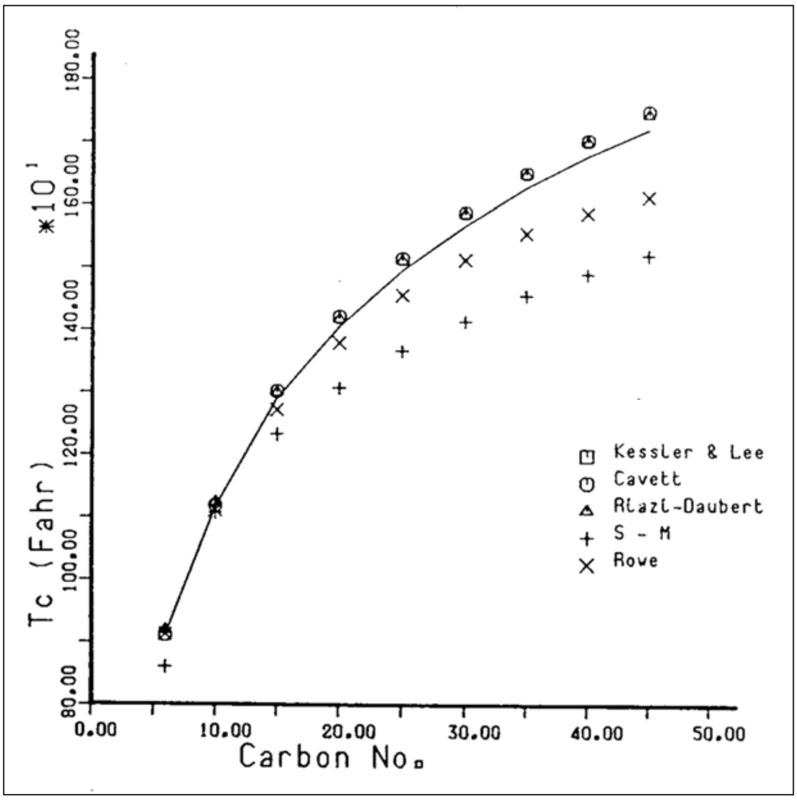
θ	a	b	c
M	4.567300 10^{-5}	2,19620	-1,0164
Tc (°R)	0.242787 10^{2}	0,58848	0,3596
Pc (psia)	3.128100 10^{-9}	-2,31250	2,3201
Vc (ft^3/lb)	7.521400 10^{-3}	0,28960	-7,6666

Heavy cut properties

Comparing the methods: Pc



Comparing the methods : Tc



- **JOBACK's method**

$$P_C = \left(0.113 + 0.0032 \cdot n_A - \sum \Delta P\right)^{-2}$$

$$V_C = 17.5 + \sum \Delta V$$

- **N_A = number of atoms in the molecule**

Groups	ΔP	ΔV
out of a cycle		
-CH3	-0,0012	65
-CH2-	0	56
>CH-	0,002	41
>C<	0,0043	27
=CH2	-0,0028	56
=CH-	-0,0006	46
>C=	0,0011	38
=C=	0,0028	36
in a cycle		
-CH2-	0,0025	48
>CH-	0,0004	38
>C<	0,0061	27
=CH-	0,0011	41
=C<	0,0008	32

Heavy cut properties

FEDOR's method

$$T_c = 535 \cdot \log \sum \Delta T$$

Groups	ΔT
-CH3	1,79
-CH2-	1,34
>CH-	0,45
>C<	-0,22
=CH2	1,59
=CH-	1,4
>C=	0,89

Viscosity modeling

Summary

Viscosity

Lohrenz-Bray-Clark's correlation

$$\rho'_C = \frac{1}{V_C} = \frac{1}{\sum_i Z_i V_{Ci}} \qquad \rho_r = \frac{\rho}{\rho'_C}$$

$$\xi_i = \frac{T_{Ci}^{1/6}}{Mw_i^{1/2} \cdot P_{Ci}^{2/3}} \qquad T_r = \frac{T}{\sum_i Z_i T_{Ci}}$$

$$\mu_i^* = \frac{34.10^{-5}\, Tr_i^{0.94}}{\xi_i} \qquad Tr_i < 1.5$$

$$\mu_i^* = \frac{17.78 \cdot 10^{-5} \left(4.58 Tr_i - 1.67\right)^{5/8}}{\xi_i} \qquad Tr_i \geq 1.5$$

Viscosity mixture @ T and low pressure

$$\mu^* = \frac{\sum_i Z_i \mu_i^* (Mw_i)^{1/2}}{\sum_i Z_i (Mw_i)^{1/2}}$$

Viscosity

Lohrenz-Bray-Clark's correlation

$$\xi = \frac{[\sum_i (Z_i T_{Ci})]^{1/6}}{[\sum_i (Z_i Mw_i)]^{1/2} \cdot [\sum_i (Z_i P_{Ci})]^{2/3}}$$

$$\mu = \mu^* + \frac{(0.1023 + a_1\rho_r + a_2\rho_r^2 + a_3\rho_r^3 + a_4\rho_r^4)^4}{\xi} - 10^{-4}$$

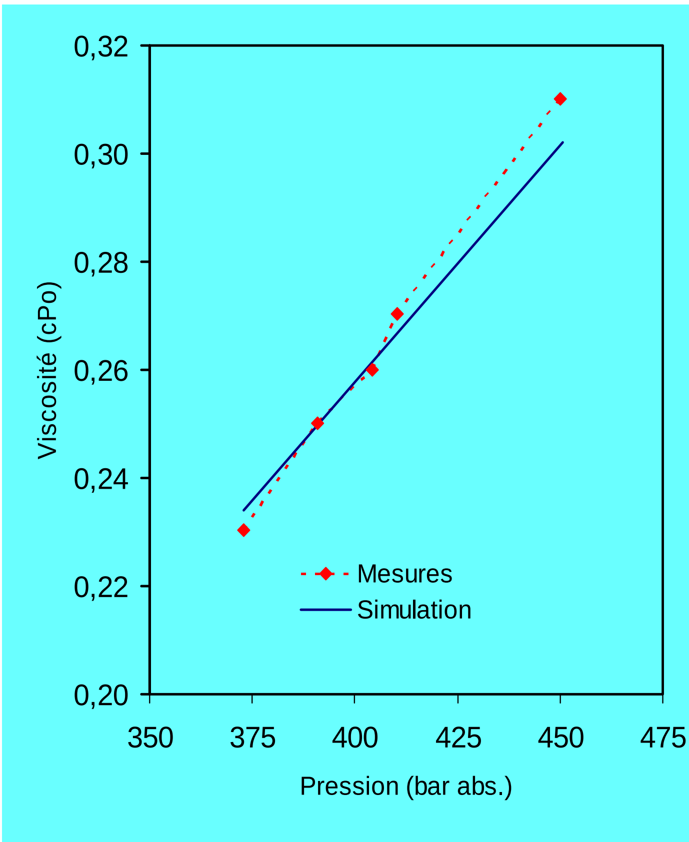
$a_1 = 0.023364 \qquad a_2 = 0.058533$

$a_3 = -0.040758 \qquad a_4 = 0.0093324$

Matching

- Liquid: Heavy cut Vc
- Vapor: Methane Vc
- If necessary: a_1, a_2, a_3, a_4

Viscosity matching



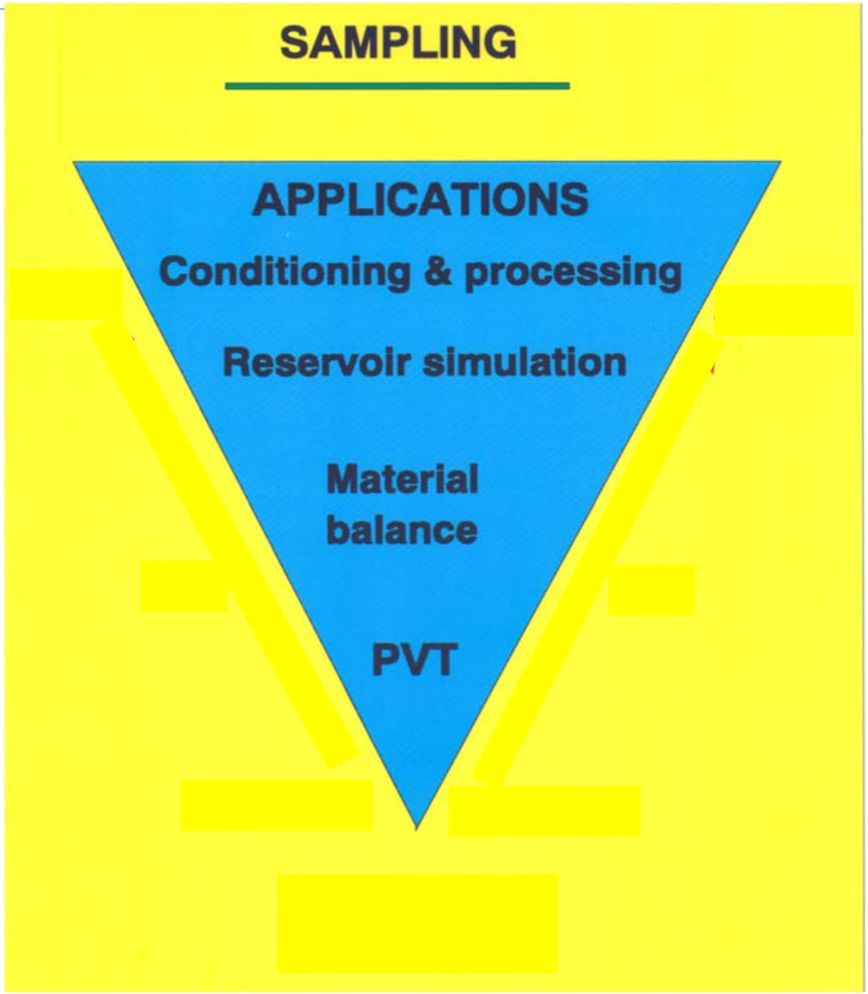
5. Measurements

Summary

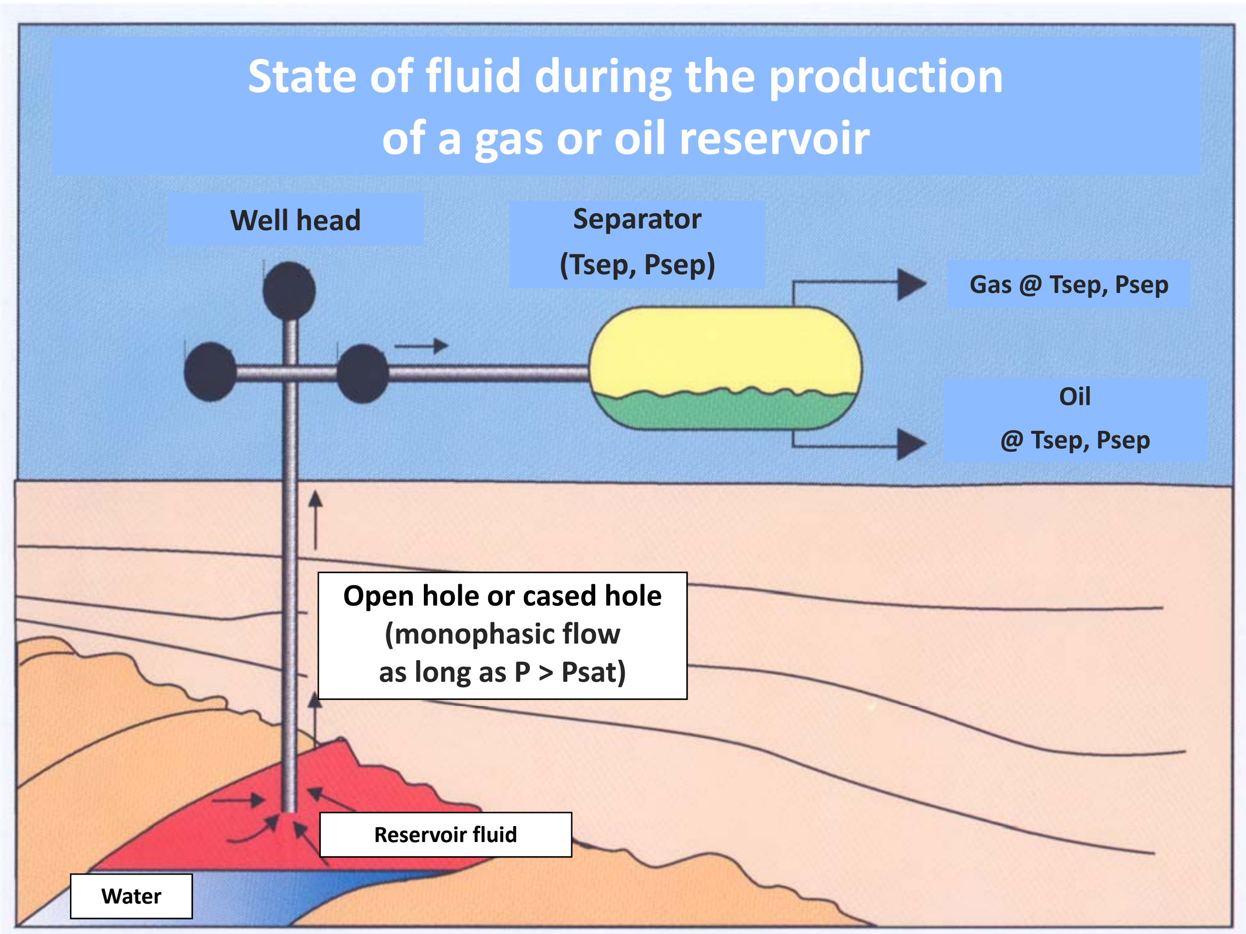
Sampling

Summary

Sampling



Sampling



Sampling

Two different groups of technique

- **Bottom hole sampling**
  - Without phase separation at the sampling point:
    - open hole: RFT, MDT, RCI, …
    - cased hole: Wireline, DST

- **Surface sampling**
  - Without phase separation at the sampling point: well head, isokinetic,
  - With phase separation: at separator conditions

RFT= Repeat Formation tester

MDT = Modular Dynamic Formation tester

DST = Drill Stem Test

Drill stem test

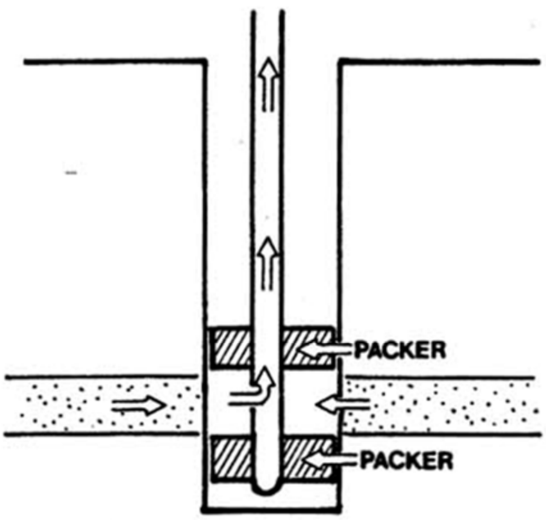
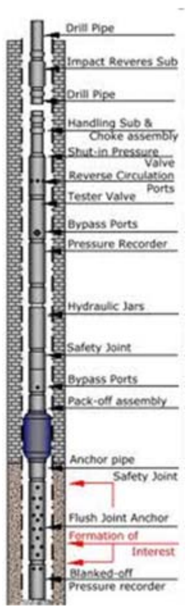
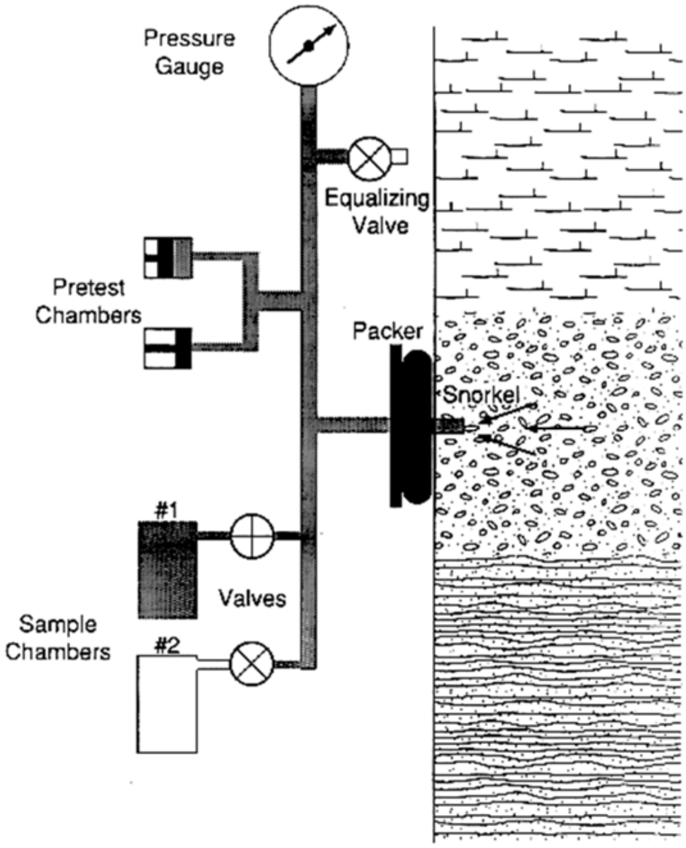
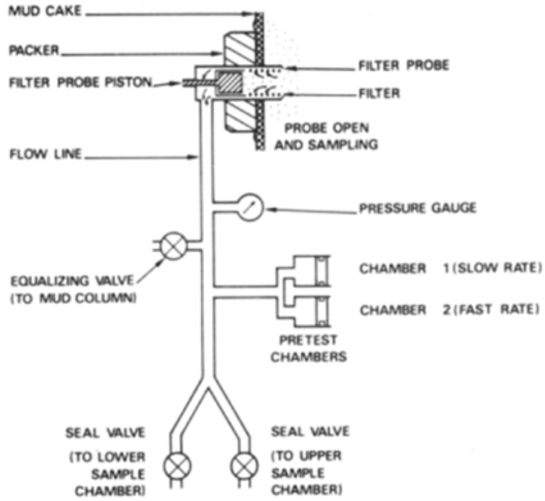


Figure 18-2 A drill stem test.



Repeat formation tester

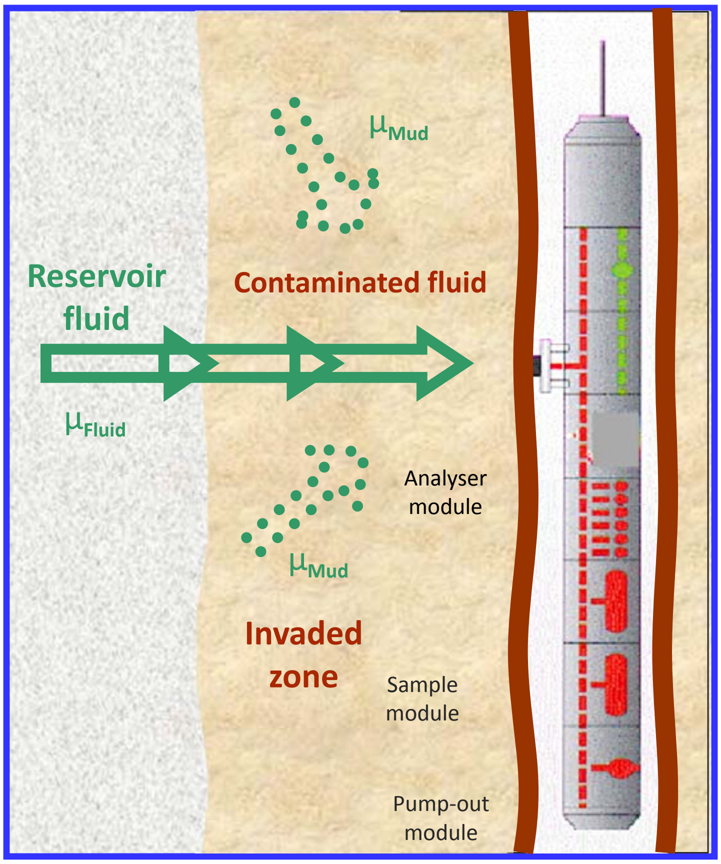




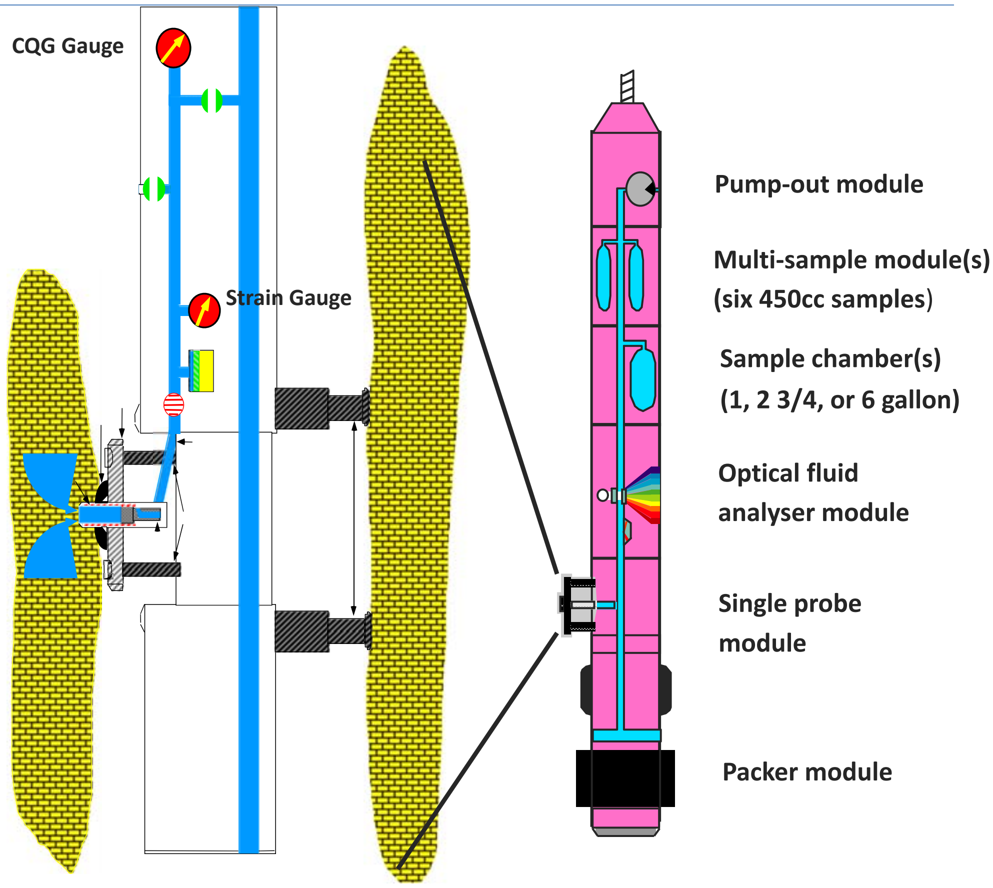
RFT Pretest and Sampling Principle
(Courtesy of Schlumberger)

Sampling

- **There is always mud filtrate invasion near the wellbore.**
- **The main problem of Open Hole sampling is to reduce the amount of filtrate in the chambers**
  → Pump out module
  → Analyzer module

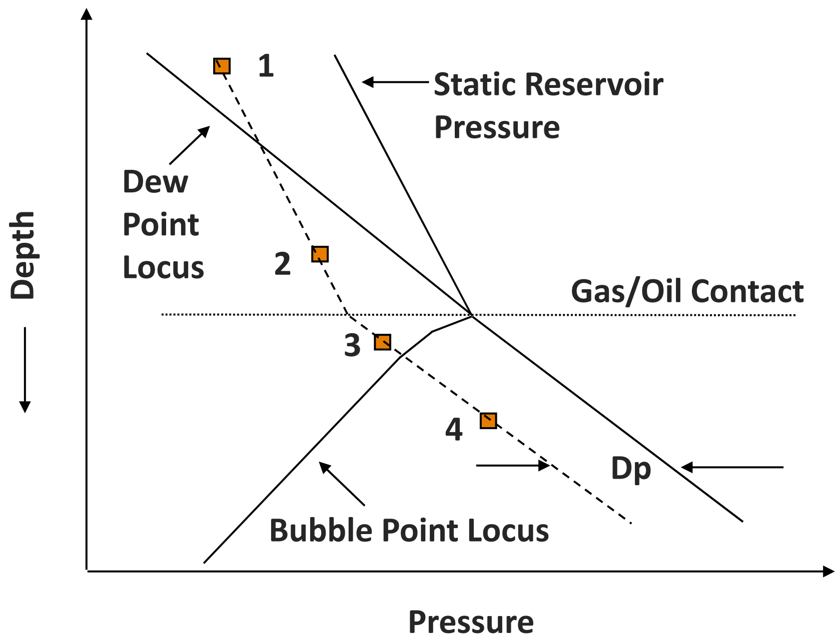


The MDT tool



Sampling

Pressure Drawdown versus sample quality



- Flowing well has pressure drop of Dp in near-wellbore region
- Sample taken at points 1 & 4 are single phase
- Sample taken at 2 & 3 are two-phase

Open Hole sampling

Advantages

- Precise depth sampling
- Characterization of the whole fluid column in one shot
- Small ΔP: monophasic sampling
- Avoid doing a DST

Drawbacks

- Contamination by mud filtrate
- Not representative for trace or aggressive components (Hg, H_2S, …)
- Small sample volume, not sufficient for crude assay
- Risk of emulsion for heavy crude

Surface sampling

Reasons

1. The difficulties in obtaining valid downhole samples in gas-condensate wells has made surface sampling at the separator the most usual method of PVT sample taking.
2. If it is known in advance what the saturation pressure of the fluid is, and it happens to be below wellhead flowing pressure (at wellhead temperature)

Drawbacks

- The PVT laboratory has to re-create the original fluid from a liquid sample and a gas sample!!!
- The risks of contamination and leakage are doubled because of this.
- The successful recombination also relies on accurate and repeatable measurements of both gas and oil rates during the test.
- These measurements may require a revision in the light of the compositional analysis.

Bottom hole or surface sampling (main points)

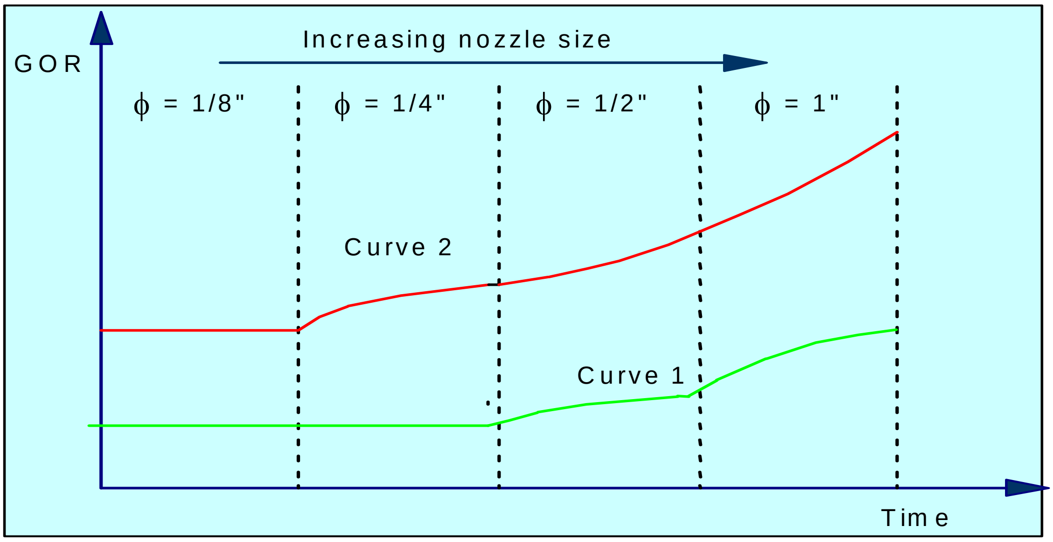
Surface

- Metering
- Stability (T, P, Qo, Qg, ...)
- Separation efficiency
- Total lift of the liquid phase

Bottom hole

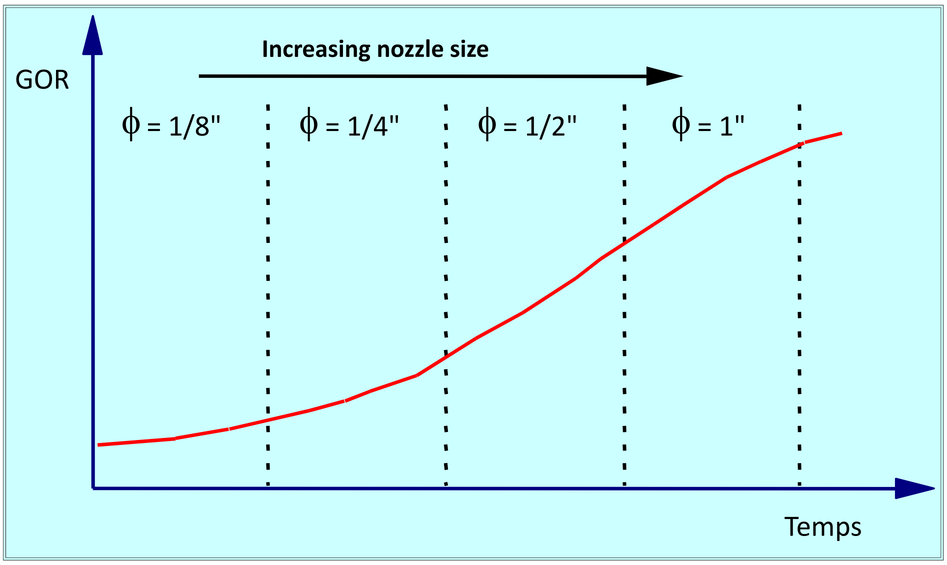
- Well conditioning (clean up, choke, flowing or shut in well, ...)
- Segregation (re opening of the well ...)
- Small sample volume

Surface sampling: oil



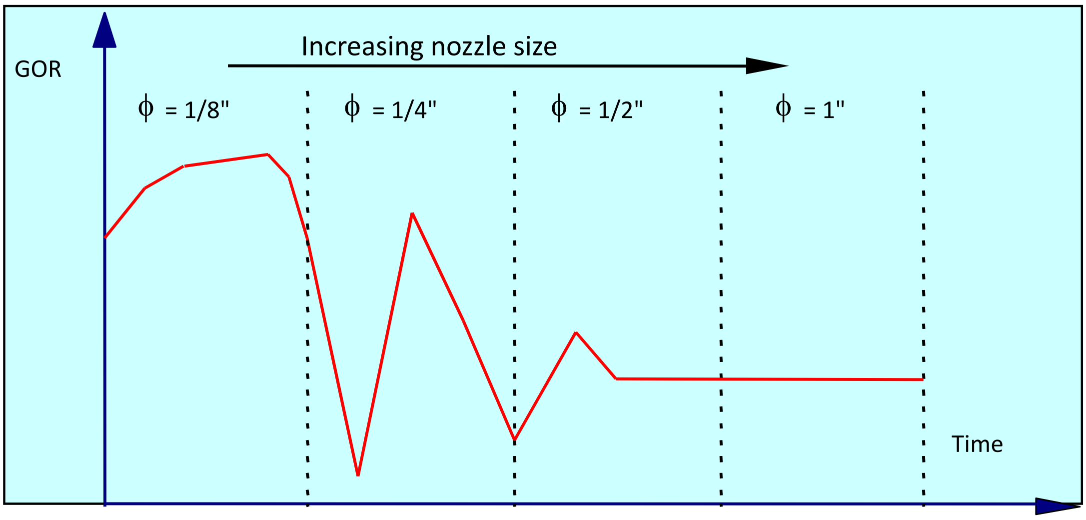
- **Constant GOR as long as:**
  - flowing pressure > bubble point pressure
- **Increasing GOR as soon as:**
  - flowing pressure = bubble point pressure

Surface sampling: saturated oil



- Whatever the choke, the GOR increases
- Surface sampling is <u>not reliable</u>

Surface sampling: gas condensate

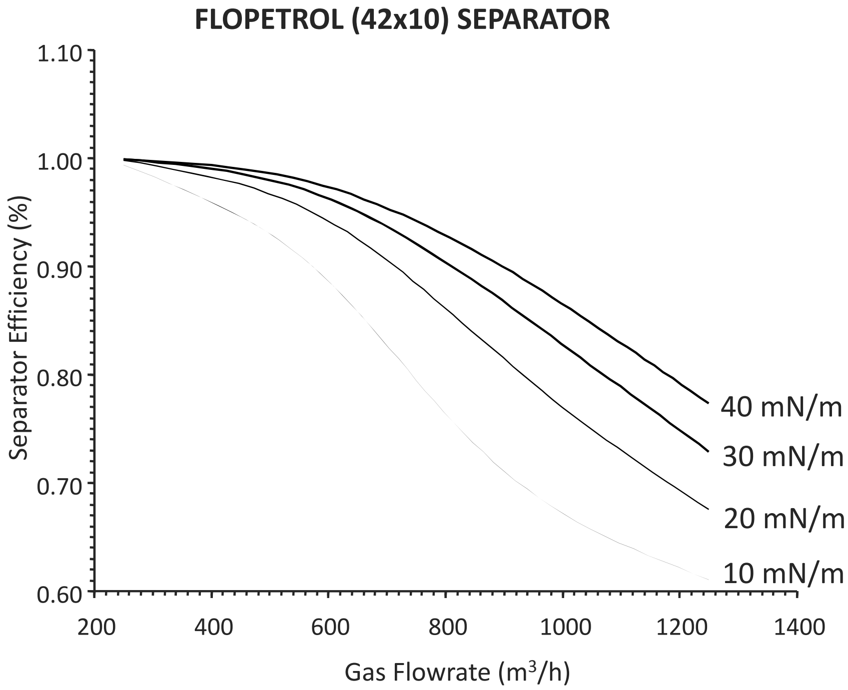


- With the 1/8'' choke, liquid accumulates at the bottom of the well: increasing GOR
- With bigger chokes, the speed of the gas raises, the accumulated liquid is carried up by the gas: the GOR decreases
- The same sequence happens again many times: zigzag curve → sluggy flow
- The flow rate must be increased (speed > 3 m/s)

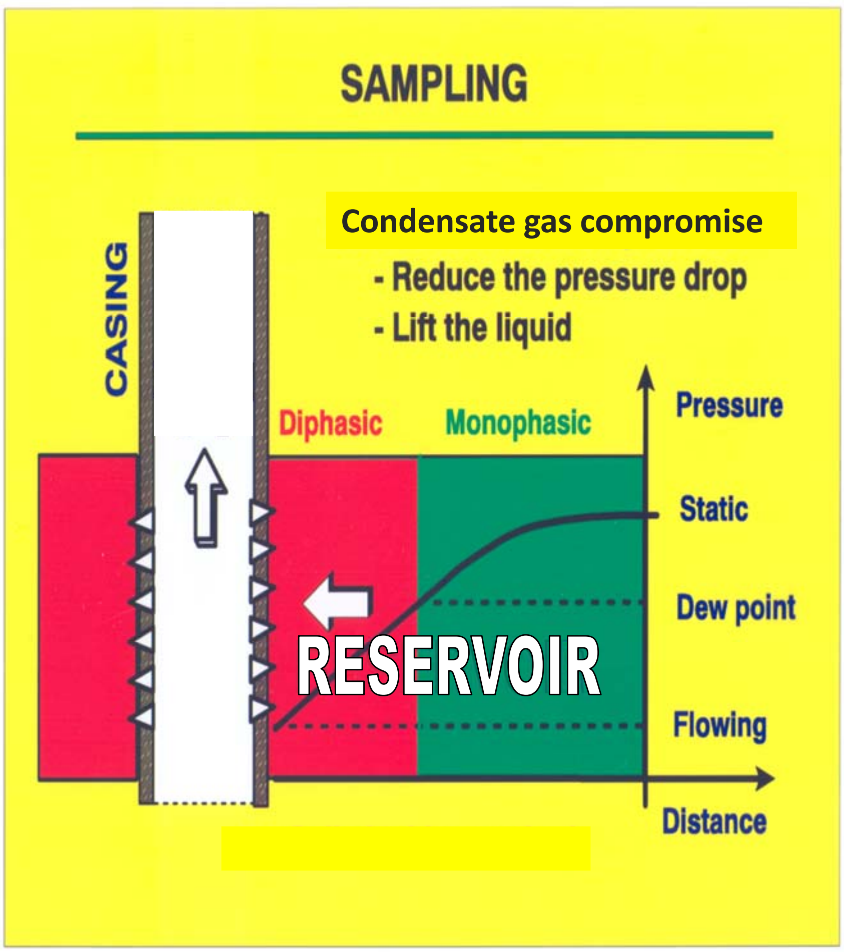
Sampling

Separator efficiency

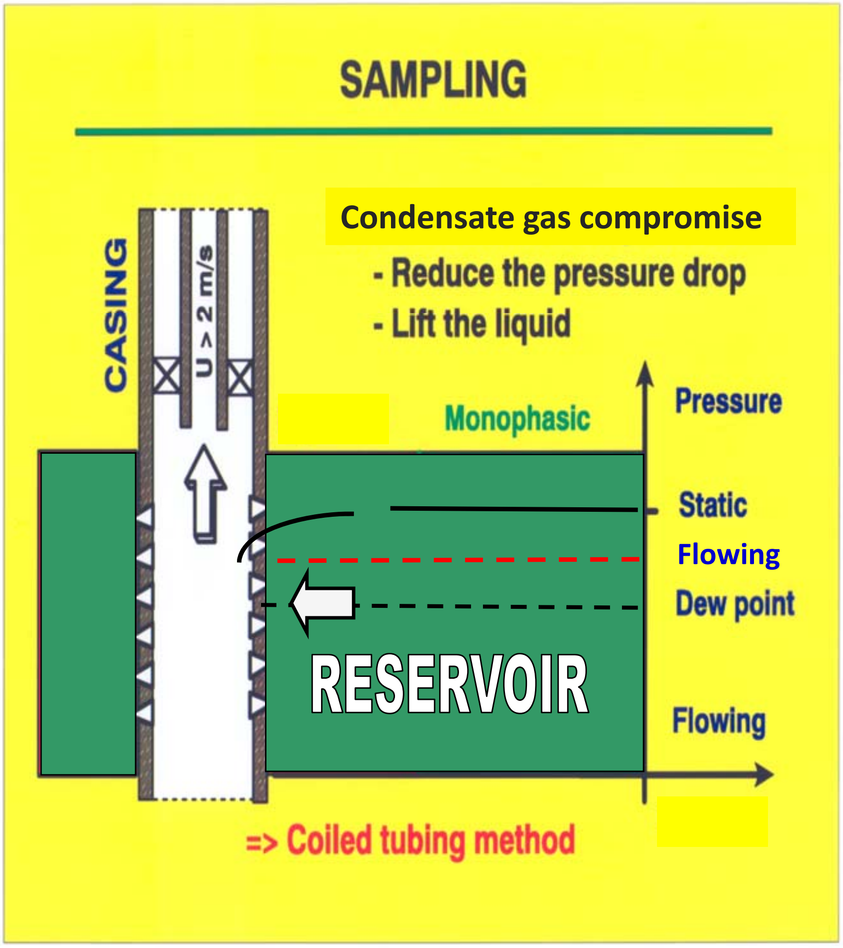
- **If the separator is not correctly sized regarding the rates being put through it:**
  - Carry over for gas condensate
  - Carry under for heavy / foamy oil



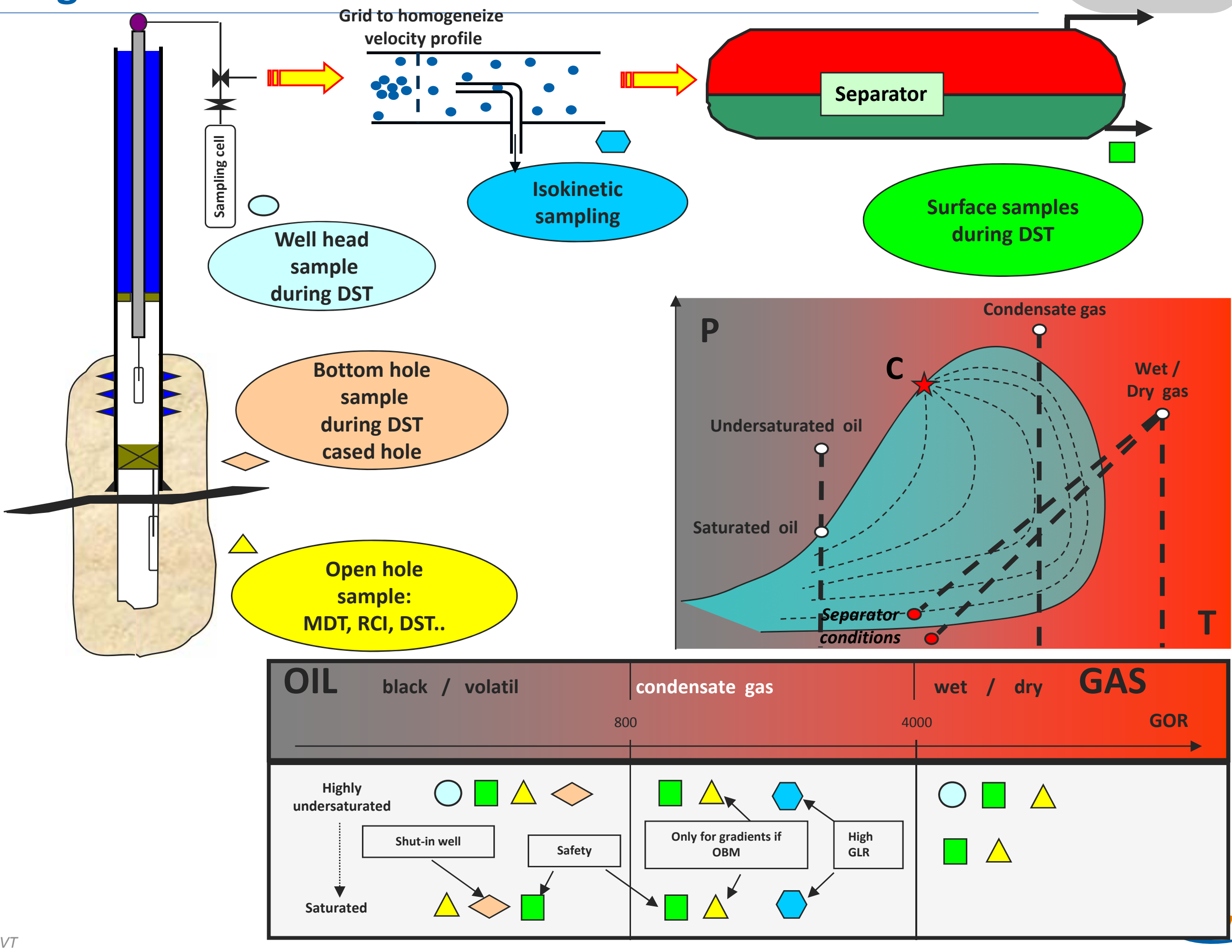
Sampling



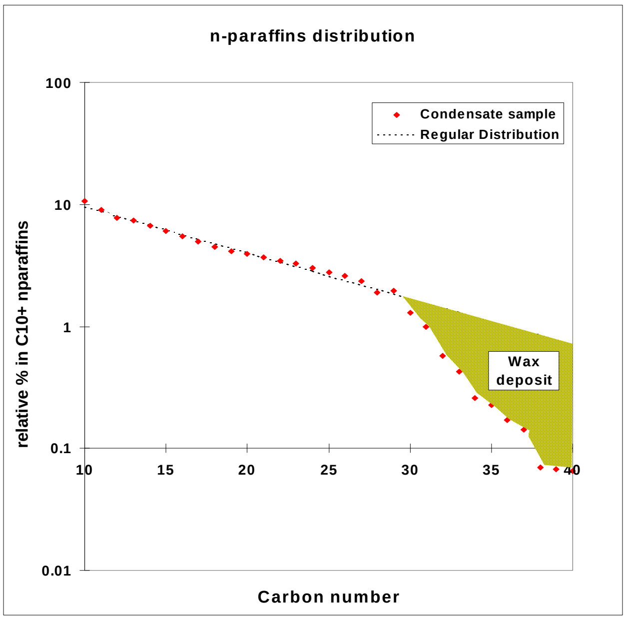
Sampling

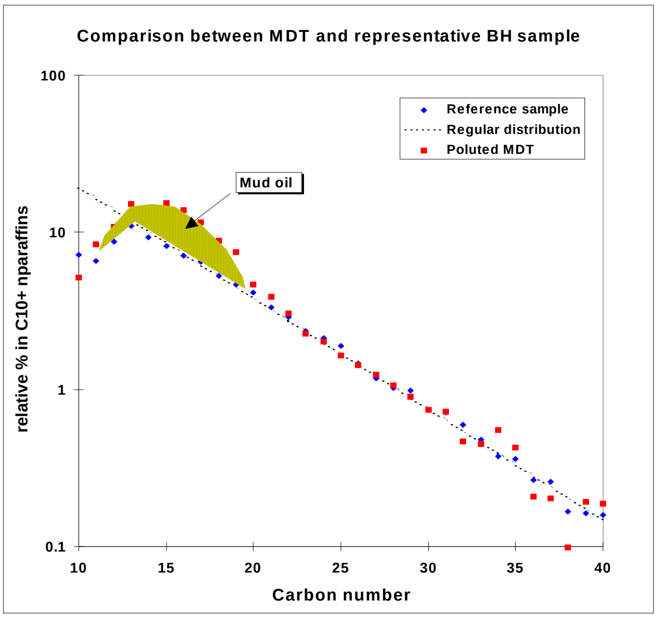


Sampling



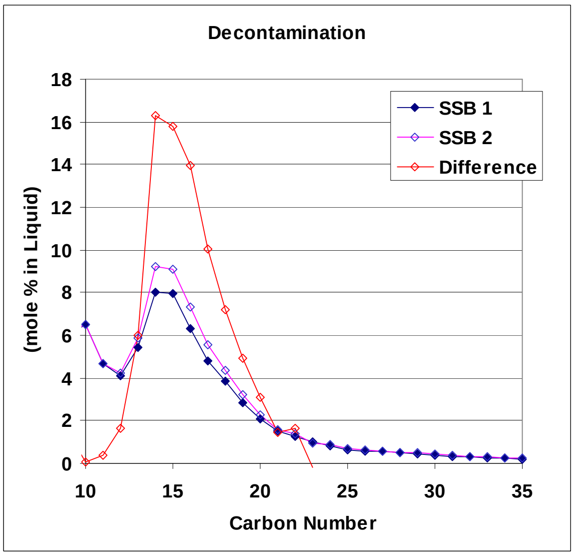
Sampling



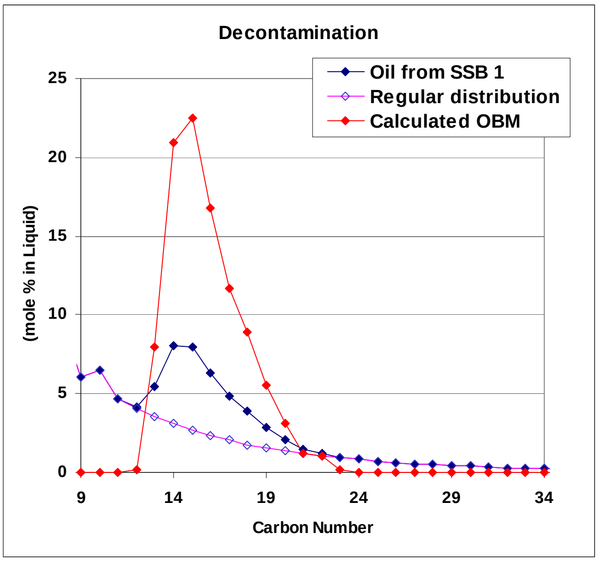


Analysis

Decontamination: composition



Composition of OBM from two samples at the same depth

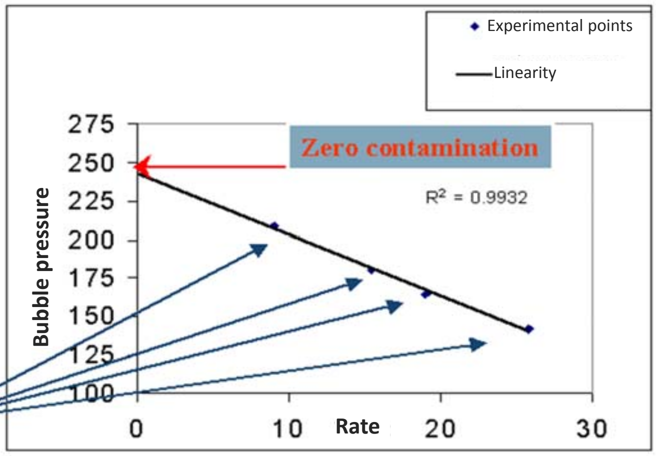


Composition of OBM from one sample based on regular HC distribution

Analysis

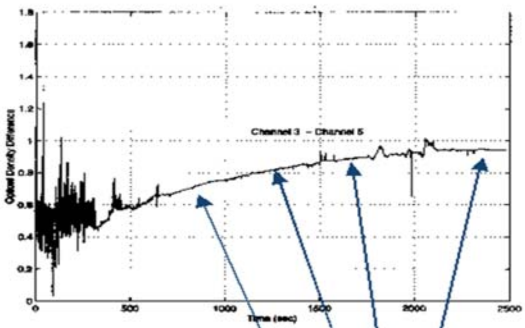
Decontamination: properties

- **Volume additivity:**
  - Mw
  - BH and Std fluid density
  - GOR
  - Bo
- **Extrapolation to zero pollution:**

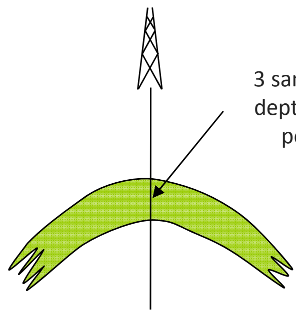


Multi contamination rates

Sampling

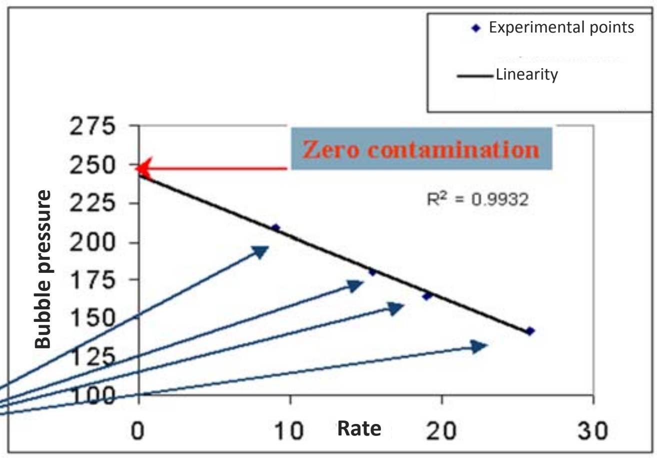


Multi sampling



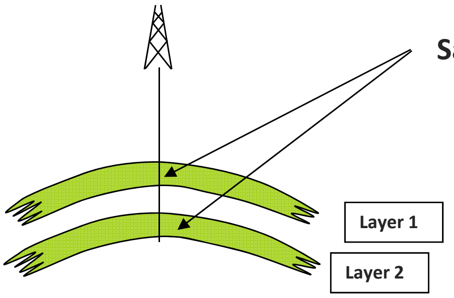
3 samples at a given depth with different pollution rates

MDT after an OBM drilling

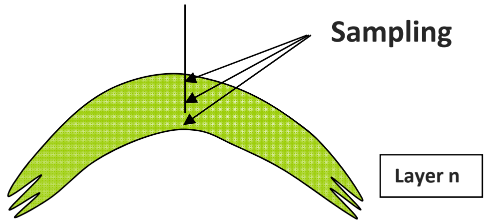


Multi contamination rates

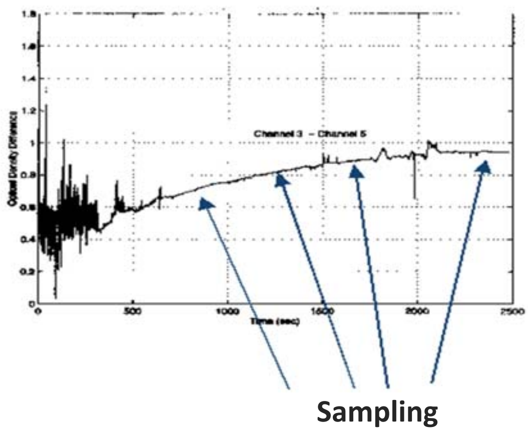
Recommendations



Connectivity?



Compositional grading?



Contamination?

Assessment of PVT Reports

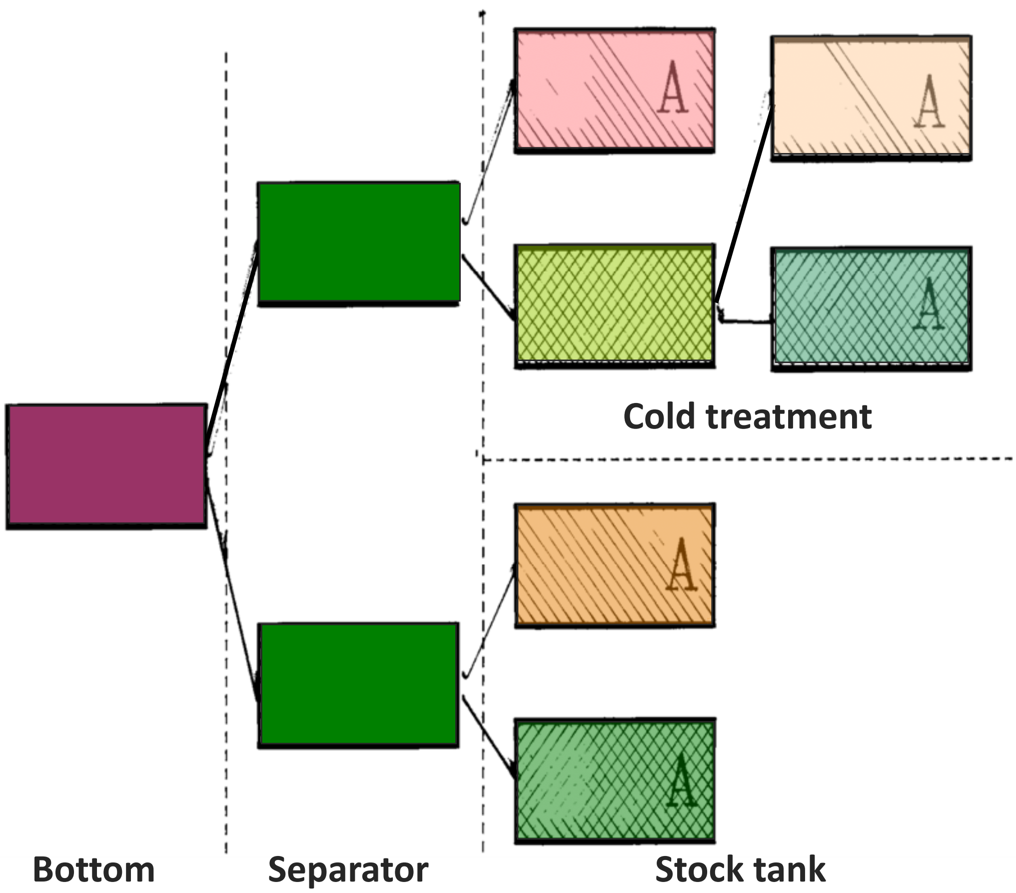
- **Sample composition check**
  - Mole percentages sum to 100?
  - Nitrogen content - possible air contamination?
  - H_2S concentration
    - was any value reported at the wellsite
    - are the lab measured values comparable

- **Mass balance check**
  - Check reservoir fluid density and composition using process, CVD or differential data

Analysis

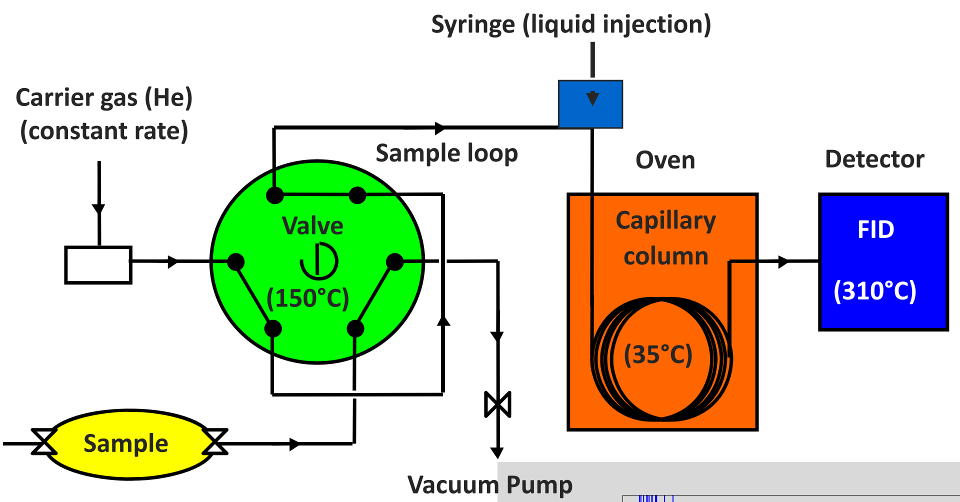
Summary

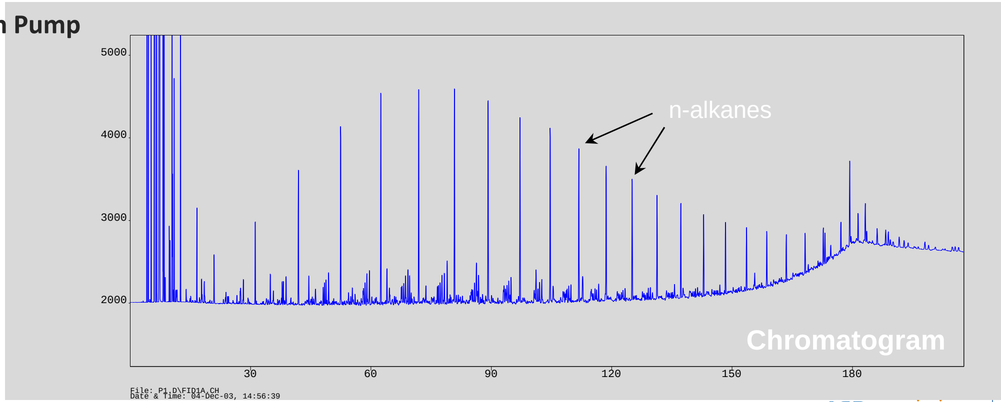
Analysis



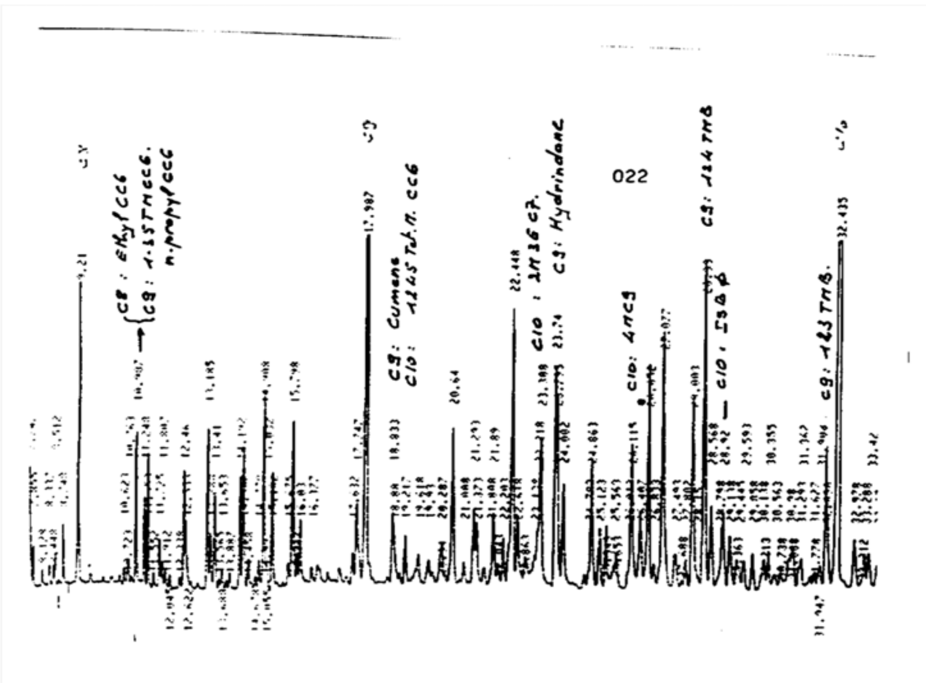
Analysis

Gas chromatography analysis





Analysis

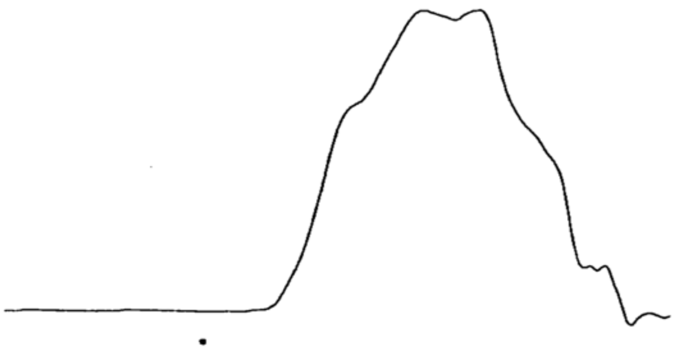


Dimethylcyclohexane
1-1-3 trimethylcyclohexane
1-1-4 trimethylcyclohexane
1 c3 c5 trimethylcyclohexane
Various naphtenes in c9
2-2-5 trimethylhexane
Para-xylene
Meta-xylene
2-3 dimethylheptane
3-4 dimethylheptane
1 c3 t5 trimethylcyclohexane
4 methyl octane
2 methyl octane
3 ethylheptane
3 methyl octane
Ortho-xylene
1-1-2 trimethylcyclohexane
Isopropylcyclohexane
1 c2 c4 trimethylcyclohexane
1 methyl t4 ethylcyclohexane
1 methyl c3 ethylcyclohexane
Normal nonane
Cumene
1 methyl c2 ethylcyclohexane
1 methyl t2 ethylcyclohexane
1 methyl 1 ethylcyclohexane
4-4 dimethyl octane
2-5 dimethyl octane
Propylbenzene
2-6 dimethyl octane
2-3 dimethyl octane
3-4 dimethyl octane
4-5 dimethyl octane
1-3 ethyl toluene
1-4 ethyl toluene
1-2 ethyl toluene
4 methyl nonane
2 methyl nonane
1-3-5 trimethylbenzene
3 methyl nonane
1-2-4 trimethylbenzene
Sec butylbenzene
Isobutylbenzene
Terbutylbenzene
Normal decane
1-2-3 trimethylbenzene

Gas chromatography

Heavy fraction characterization

GPC analysis



C11 fraction	2.823
C12/13 fraction	4.608
C14/15 fraction	3.612
C16/17 fraction	2.711
C18/19 fraction	2.092
C20/24 fraction	3.207
C25/29 fraction	1.802
C30/39 fraction	1.945
C40/49 fraction	.818
C50/74 fraction	.615
C75/99 fraction	.180
C100/149 fraction	.039
C150/200 fraction	.007
C200/249 fraction	.003

"Heavy" fraction
Criteria → Process

Boiling point →
Distillation or gas chromatography

Molecular weight →
Gel permeation chromatography

Chemical family →
Liquid Chromatography

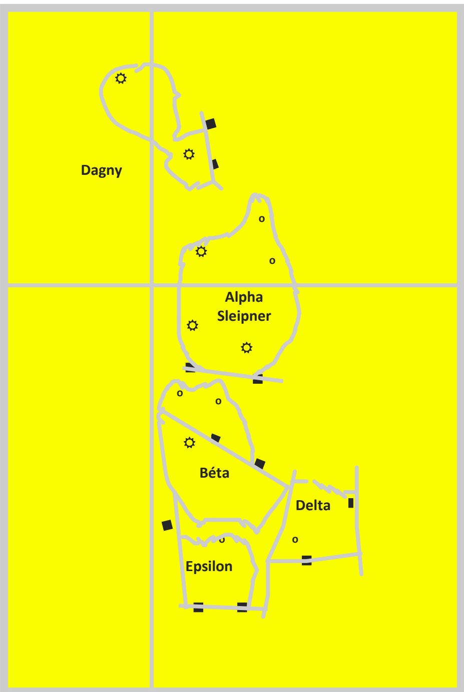
Functional group →
Absorption spectrometry

6. Fluid synthesis

Summary

Fluid synthesis

**Data from:
geology, geochemistry,
production, PVT studies...**



→

**Tool
box**

↓

Reservoir connectivity

Properties profiles

Contact location

Fluid model(s)

Fluid synthesis

Tool box

- Samples expertise
- Data standardization
- Statistical analysis
- EOS fluid model
- Static gravitational model
- GWD (gas show)

Light ends lumping methods

C6 cut: lumping according to boiling temperature (36.5<Teb<69.2 °C)

Composants	M	Tc	Pc	w	Teb	% mol.
Cyclopentane	70,14	511,6	45,09	0,1923	322,05	0,0887
2-2 dimethyl butane	86,18	488,7	30,80	0,2310	322,85	0,0088
2-3 dimethyl butane	86,18	499,9	31,31	0,2473	331,15	0,0299
2 methyl pentane	86,18	497,5	30,10	0,2791	333,35	0,2629
3 methyl pentane	86,18	504,5	31,21	0,2750	336,35	0,1576
Normal hexane	86,18	504,4	29,69	0,2957	341,25	0,5191
C6 (Teb)	*84,85*	*503,1*	*30,87*	*0,2781*		*1,0670*

C6 cut : lumping according to carbon number

Composants	M	Tc	Pc	w	Teb	% mol.
2-2 dimethyl butane	86,18	488,7	30,80	0,2310	322,85	0,0088
2-3 dimethyl butane	86,18	499,9	31,31	0,2473	331,15	0,0299
2 methyl pentane	86,18	497,5	30,09	0,2791	333,35	0,2629
3 methyl pentane	86,18	504,5	31,21	0,2750	336,35	0,1576
Normal hexane	86,18	504,4	29,69	0,2957	341,25	0,5191
Methylcyclopentane	86,18	532,7	37,90	0,2395	344,95	0,2628
Benzène	78,11	562,1	48,94	0,2100	353,25	0,2969
Cyclohexane	84,16	553,4	40,73	0,2144	353,85	0,4549
C6 (CN)	*84,25*	*523,3*	*35,15*	*0,2521*		*1,9929*

M: molecular weight	**g/mol**
Tc: critical temperature	**Kelvin**
Pc: critical pressure	**bar**
ω: acentric factor	**dimensionless**
Teb: boiling point temperature	**Kelvin**

Calculation of mixture properties

$$T_C = \frac{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{Z_i Z_j T_{C_i} T_{C_j}}{\sqrt{P_{C_i} P_{C_j}}}}{\displaystyle\sum_{i=1}^{n}\frac{Z_i T_{C_i}}{P_{C_i}}}$$

$$k_{nm} = \frac{\displaystyle\sum_{i=L_n}^{U_n}\sum_{j=L_m}^{U_m} z_i z_j M_i M_j k_{ij}}{\overline{M}_n \overline{M}_m \displaystyle\sum_{i=L_n}^{U_n} z_i \sum_{j=L_m}^{U_m} z_j}$$

$$P_C = \frac{T_C}{\displaystyle\sum_{i=1}^{n}\frac{Z_i T_{C_i}}{P_{C_i}}}$$

$$\omega = \sum_{i=1}^{n} Z_i \omega_i$$

Pure components and light cuts

Pure compounds

Components	M	Tc	Pc	ω	% mol.
N2	28.01	126.2	33.94	0.0400	0.326
CO2	44.01	304.2	73.76	0.2250	2.590
C1	16.04	190.6	46.00	0.0115	64.685
C2	30.07	305.4	48.84	0.0908	8.998
C3	44.10	369.8	42.46	0.1454	5.118
iC4	58.12	408.1	36.48	0.1760	0.737
nC4	58.12	425.2	38.00	0.1928	2.035

Lumping according to the carbon number

Components	M	Tc	Pc	ω	% mol.
iC5	71.91	465.42	34.39	0.2231	0.754
nC5	72.15	469.60	33.74	0.2273	0.902
C6	84.25	623.33	35.15	0.2521	1.993
C7	97.46	558.34	32.98	0.2801	2.048
C8	111.24	586.58	29.01	0.3180	1.467
C9	125.80	610.23	26.29	0.3710	0.993
C10	139.16	635.02	24.82	0.4101	0.808

Lumping according to boiling point temperature

Components	M	Tc	Pc	ω	% mol.
iC5	72.15	460.36	33.84	0.2272	0.666
nC5	72.15	469.6	33.74	0.2273	0.902
C6	84.85	503.13	30.87	0.2781	1.067
C7	90.53	538.64	34.31	0.2683	1.905
C8	103.57	572.13	31.33	0.2817	2.084
C9	118.09	601.84	28.05	0.3523	1.130
C10	133.72	633.17	26.33	0.3851	1.211

Data standardization

	GECO		ELF		CORELAB	
N2	0.37		0.35		0.36	
CO2	2.65		2.59		2.67	
C1	66.18		64.69		65.69	
C2	9.02		9.00		9.03	
C3	4.93		5.12		4.89	
iC4	0.72		0.74		0.70	
nC4	2.01		2.04		1.86	
iC5	0.67		0.75		0.6	
nC5	0.95		0.90		0.86	
C6	1.15		1.99		1.10	
C7	1.86		2.05		1.84	
C8	1.95		1.47		2.08	
C9	1.15		0.99		1.25	
C10+	6.38		7.35		7.07	
MC10+	272		236		255	

Measurements: analysis

"Heavy" fraction
Criteria → Process

Boiling point →
Distillation or gas chromatography

Molecular weight →
Gel permeation chromatography

Chemical family →
Liquid Chromatography

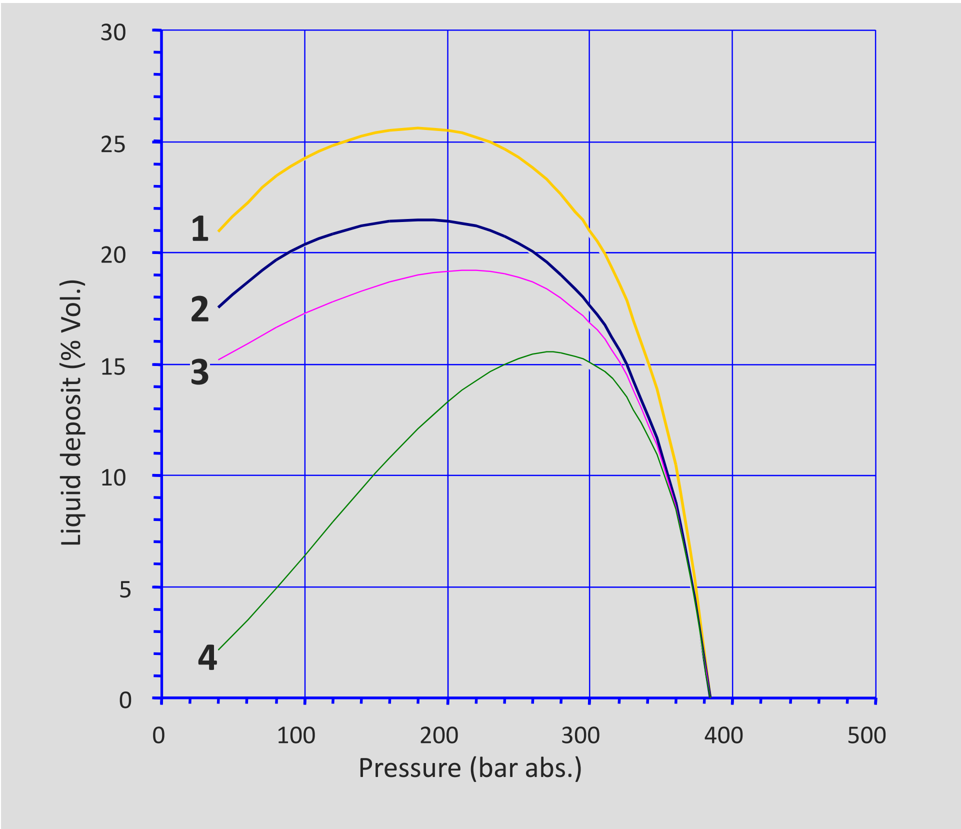
Functional group →
Absorption spectrometry

Data standardization

	GECO		ELF		CORELAB	
N2	0.37	0.37	0.35	0.35	0.36	0.36
CO2	2.65	2.62	2.59	2.59	2.67	2.65
C1	66.18	65.42	64.69	64.69	65.69	65.06
C2	9.02	8.92	9.00	9.00	9.03	8.94
C3	4.93	4.87	5.12	5.12	4.89	4.84
iC4	0.72	0.71	0.74	0.74	0.70	0.69
nC4	2.01	1.99	2.04	2.04	1.86	1.84
iC5	0.67	0.66	0.75	0.75	0.6	0.59
nC5	0.95	0.94	0.90	0.90	0.86	0.85
C6	1.15	1.13	1.99	1.07	1.10	1.08
C7	1.86	1.84	2.05	1.91	1.84	1.93
C8	1.95	1.94	1.47	2.08	2.08	2.13
C9	1.15	1.14	0.99	1.13	1.25	1.27
C10+	6.38	7.46	7.35	7.76	7.07	7.76
MC10+	272	236	236	236	255	236

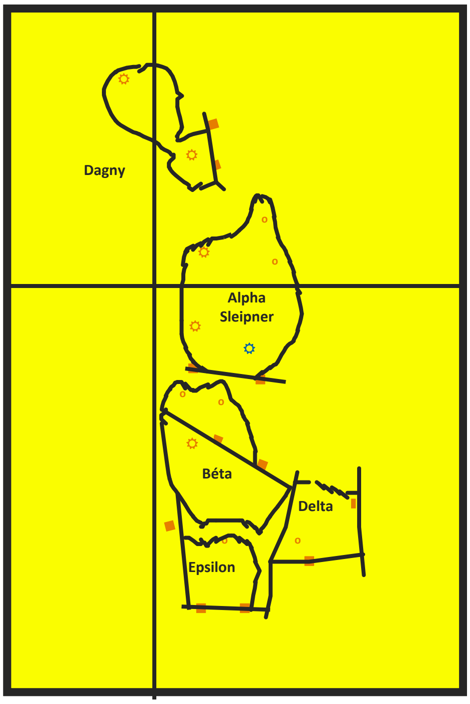
Same lumping method - same Mw for the heavy cut (C10+)

Liquid deposit



1: CM E (V @ P init)
2: CM E (V @ P dew)
3: CVD (V @ P dew)
4: CM E (V @ P)

Field cases



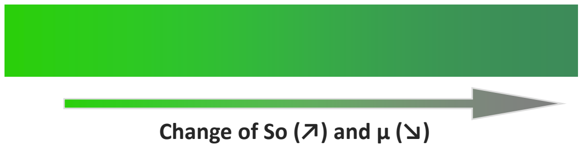
7. Gas injection

Summary

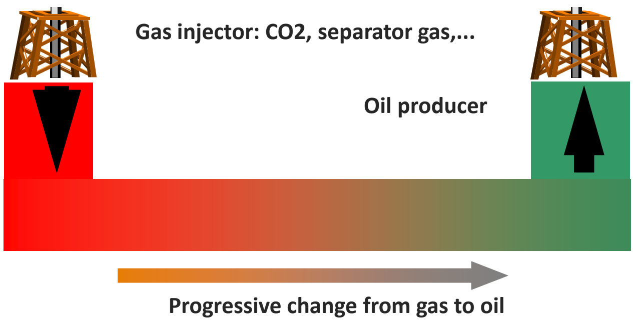
Specific PVT experiments

Summary

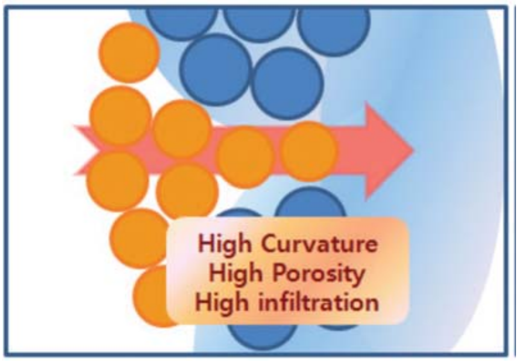
Mechanisms



- According to gas and oil composition also reservoir conditions:
- No miscibility: two phases → sweeping efficiency depends on mobility ratio.

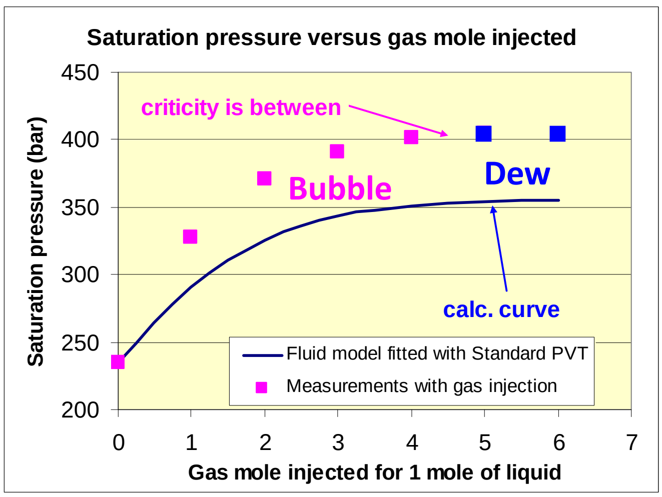


- According to gas and oil composition also reservoir conditions:
  - No miscibility: one phase → swelling effect depends on the undersaturated oil in the reservoir.



- According to gas and oil composition also reservoir conditions:
  - Miscibility is possible: obtaining of a progressive change → means Criticality.

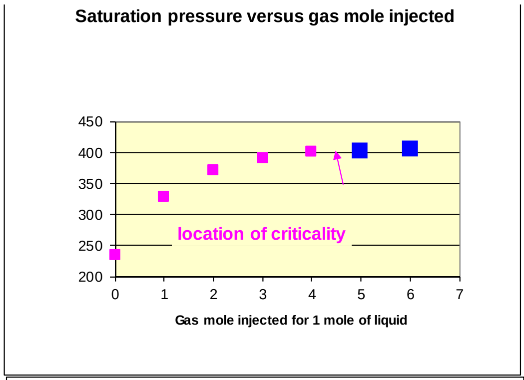
- Oil: 40°API, BPP = 235 b, BHP = 360 b
- First matching on standard oil only measurements
- Experiment: gas separator injection in oil for several steps, bubble points measured
  - The model based on standard measurements is wrong
  - Phenomena are not well represented (L/V, composition, …)
  - Necessity to take into account the effect of gas injection.
- Need for gas injection experiments, which represent the right phenomena: Miscibility and Criticality

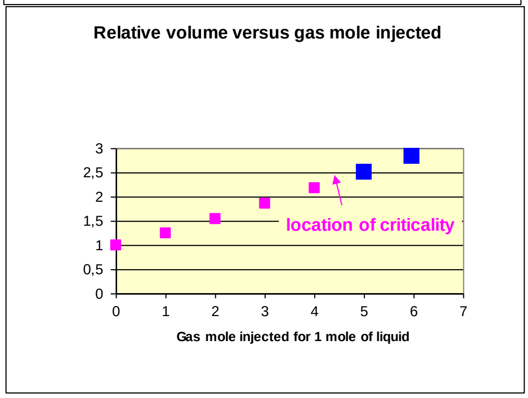


Gas injection

Specific PVT experiment

- **Swelling test**
  Gas is added to the initial reservoir fluid, mixture is kept monophasic (increasing of exp. pressure)
  - Saturation pressure profile
  - Criticality location
  - Relative volume (swelling effect)





⇨ **No phase separation, no material balance**

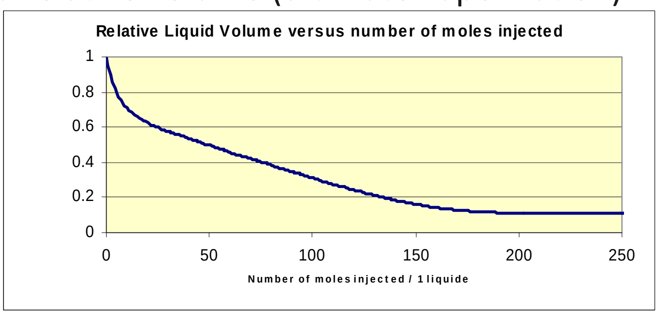
⇨ **Approach of criticality location**

⇨ **Standard PVT for each mixture**

Gas injection

Specific PVT experiment

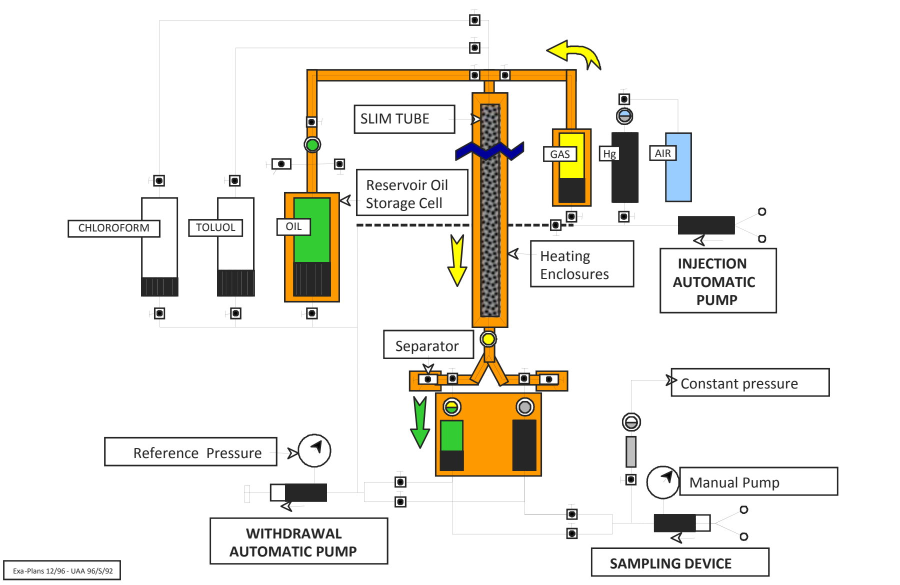
- **Multiple contact test (MCT)**
  Gas is added at constant pressure: equilibrium
  - One phase is withdrawn (gas or liquid)
  - Compositional profile
  - Liquid relative volume (ultimate vaporization)



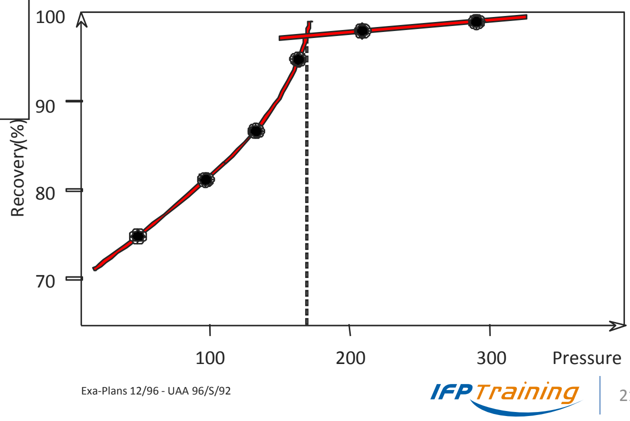
- **Represent the reservoir around injector**

⇨ **Experimental problems: equilibrium should be reached, phase separation V/L, Mat. Balance**

Slim tube



Miscibility conditions: MCMP

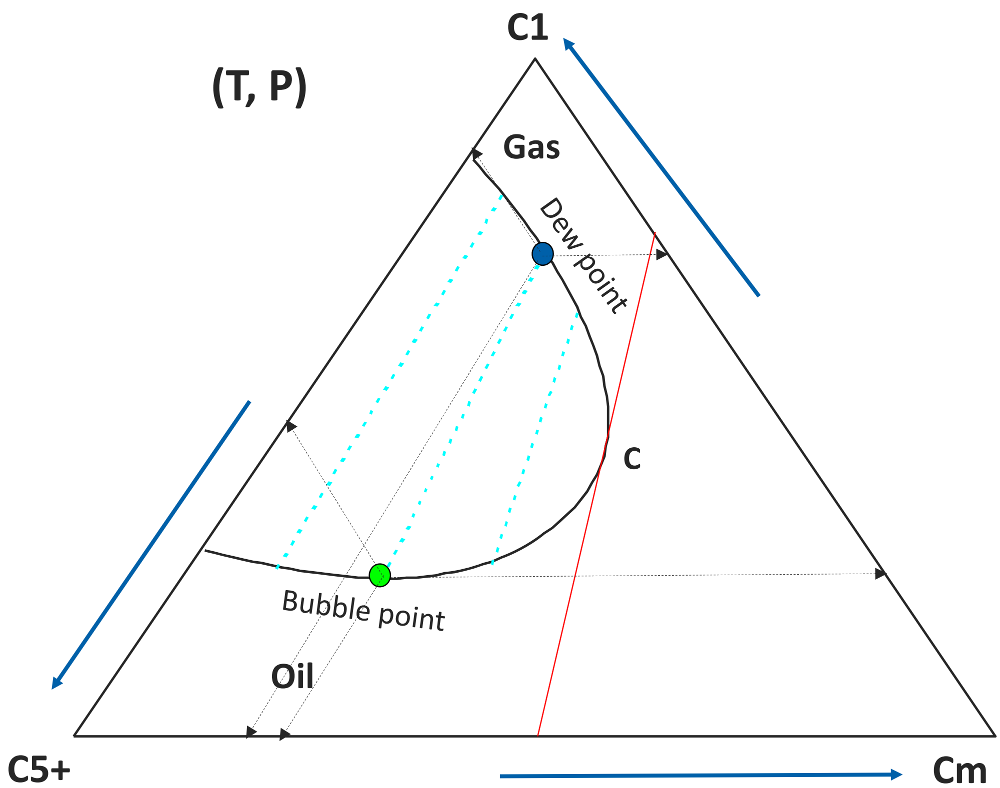


Miscibility (FCMP, MCMP, Kr...)

Summary

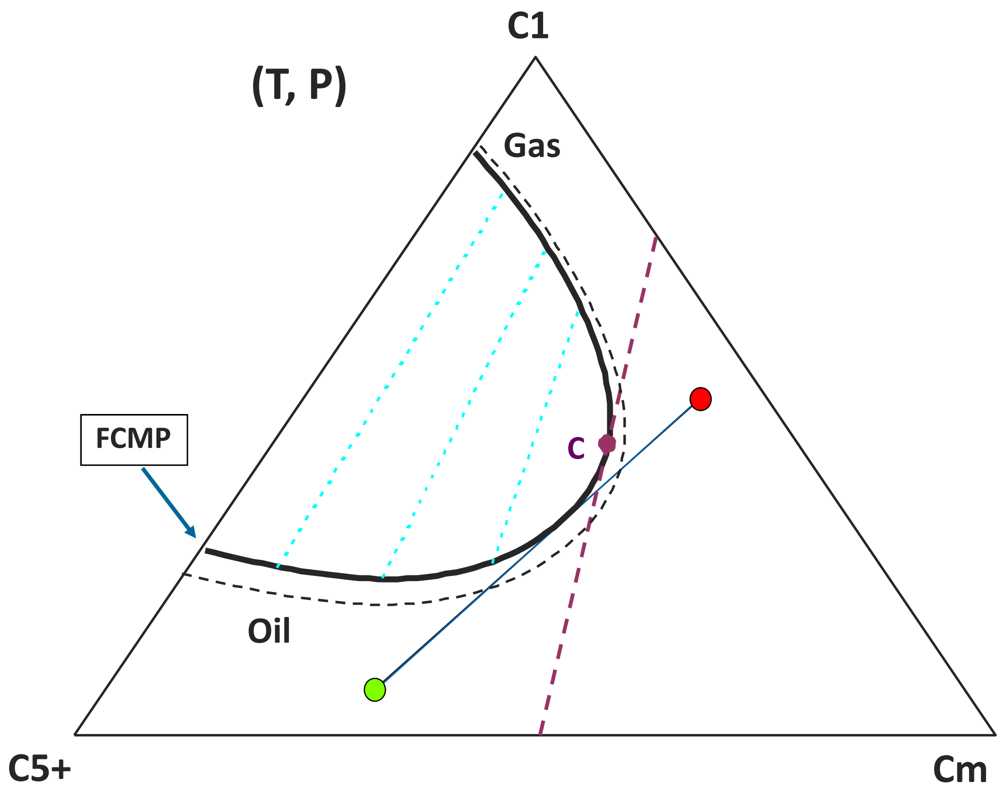
Miscibility

Ternary diagram



Miscibility

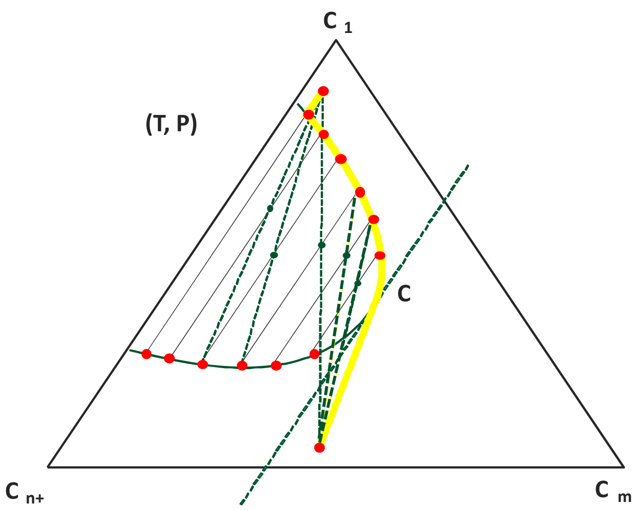
First Contact Miscibility (FCMP)

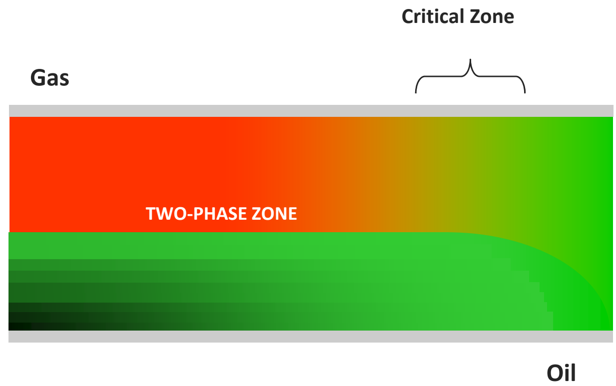


Minimum Miscibility Pressure

Miscibility

Multiple Contact Miscibility

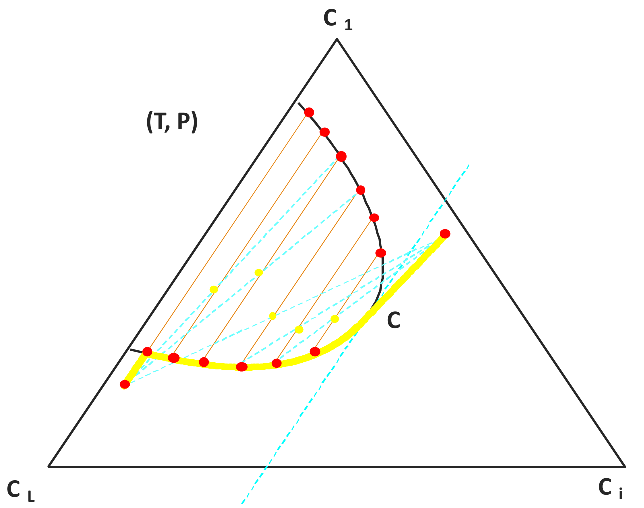


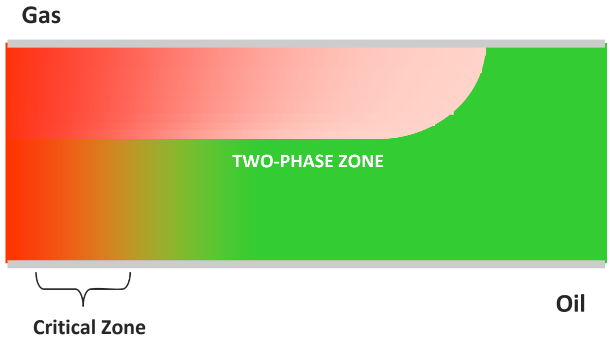


"Front" miscibility (vaporizing gas drive)

The front gas vaporizes the oil intermediate components: gas becomes heavier & miscible

Multiple Contact Miscibility

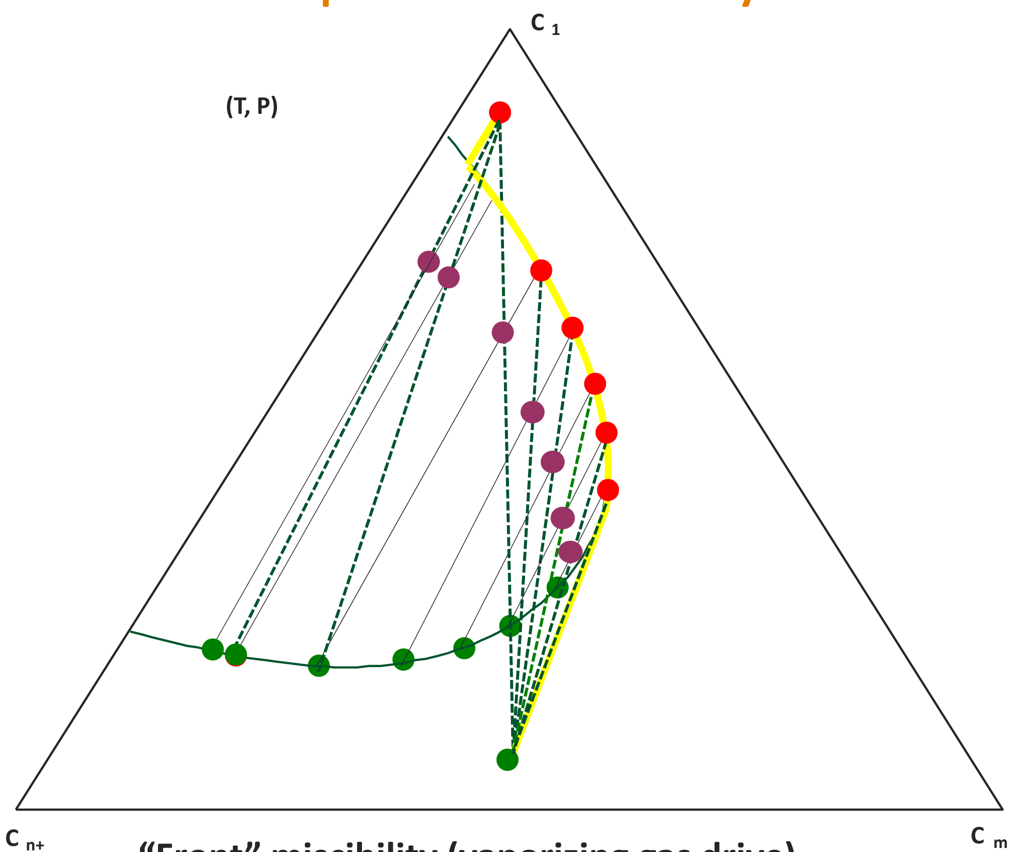




"Rear" miscibility (condensing gas drive)

The rear gas intermediate components condense in the oil: oil becomes lighter & miscible

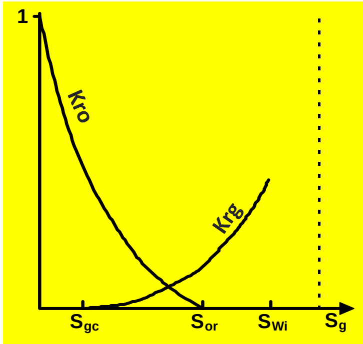
Multiple Contact Miscibility



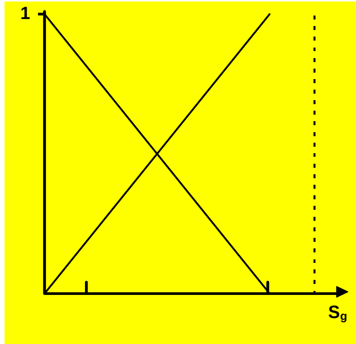
"Front" miscibility (vaporizing gas drive)

Miscible model

- **Interfacial tension:**



No-miscible



Miscible

- **The following are modeled:**

$$\begin{cases} K_{rog} = F(\sigma)K_{rog_{nm}} + (1 - F(\sigma))K_{rog_m} \\ K_{rg} = F(\sigma)K_{rg_{nm}} + (1 - F(\sigma))K_{rg_m} \end{cases}$$

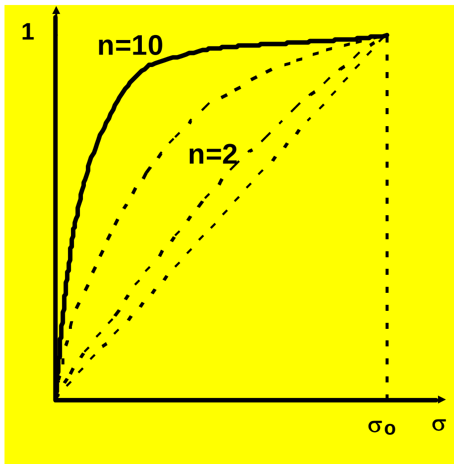
$$with \;\; F(\sigma) = \left(\frac{\sigma}{\sigma_0}\right)^{1/n}$$

$$\left.\begin{array}{l} \sigma_0 \approx 1 dyne/cm \\ n = 2 \end{array}\right\} \textit{to be adjusted according to the situation}$$

Miscible model

- **Interfacial tension:**
  - High values of n (10, 15) correspond to cases of low miscibility
  - For capillary pressure, Pcgo, the following equation is used:

$$\mathbf{P_{cgo} = P_{cgonm}\left(\frac{\sigma}{\sigma_o}\right)}$$



- **The flowrates are therefore proportional to the saturations**

Compositional matching

Summary

Gas injection

Matching

- **Specific PVT experiments are performed:**

Swelling test Multiple Contacts Test (MCT)

Specific matching methodology

- **Initial oil**
  Classical volumetric matching:
  - Tc, Pc, ω of the heavy cut(s),
  - interaction between the C1 and the heavy cut(s),
  - volume shift.
- **Equilibrium data**
  Matching of equilibrium data:
  - Interactions between the heavy cut(s) and all the other components.

8. Interfacial Tension

Summary

Interfacial tension

Sugden and Mac Leod's method (pure components)

$$\sigma = \left(Pa \cdot \frac{\rho_L - \rho_V}{M} \right)^4$$

ρ_L: Liquid phase density	g/cm^3
ρ_V: Vapor phase density	g/cm^3
M: Molecular weight	g/mole
Pa: Parachor	$(dyne/cm)^{1/4}$. $cm^3/mole$
σ: Interfacial tension	dyne / cm

The parachor (from the greek para(close to) and chor (space)) is a name created by Sugden and is an empirical constant that links the surface tension of a liquid to its molecular volume. It may be used to compare molecular volumes under the condition where they have the same surface tension.

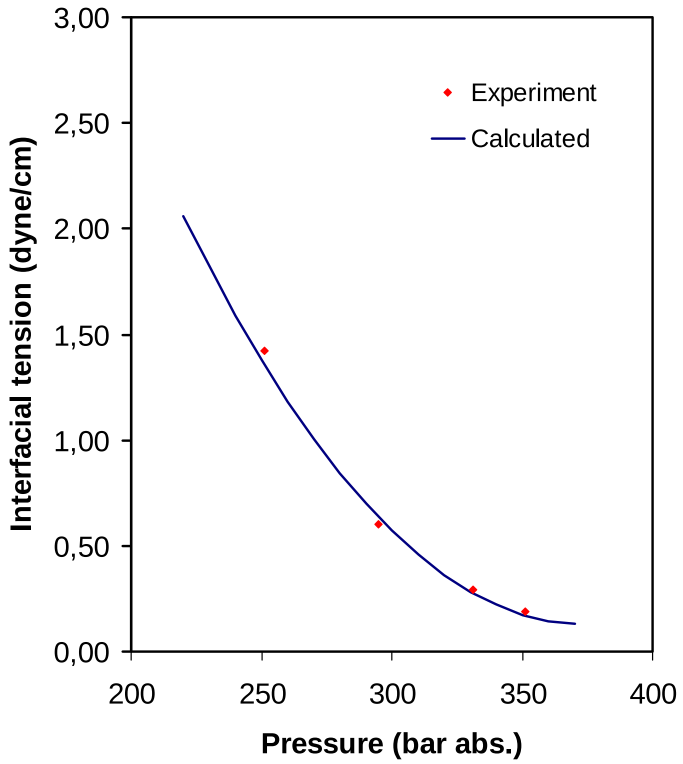
Interfacial tension

Sugden and Mac Leod's method (mixtures)

$$\sigma = \left\{ \sum_{i=1}^{n} Pa_i \cdot \left(x_i \frac{\rho_L}{M_L} - y_i \frac{\rho_V}{M_V} \right) \right\}^4$$

X_i, Y_i: Molar fraction of component i in the liquid and vapor phases
ρ_L, ρ_V: Liquid and vapor phase densities *g/cm³*
M_L, M_V: Molecular weight of liquid and vapor phases *g/mole*
Pa_i: Parachor of component i *(dyne/cm)$^{1/4}$. cm³/mole*
σ: Interfacial tension *dyne/cm*

Matching of interfacial tension



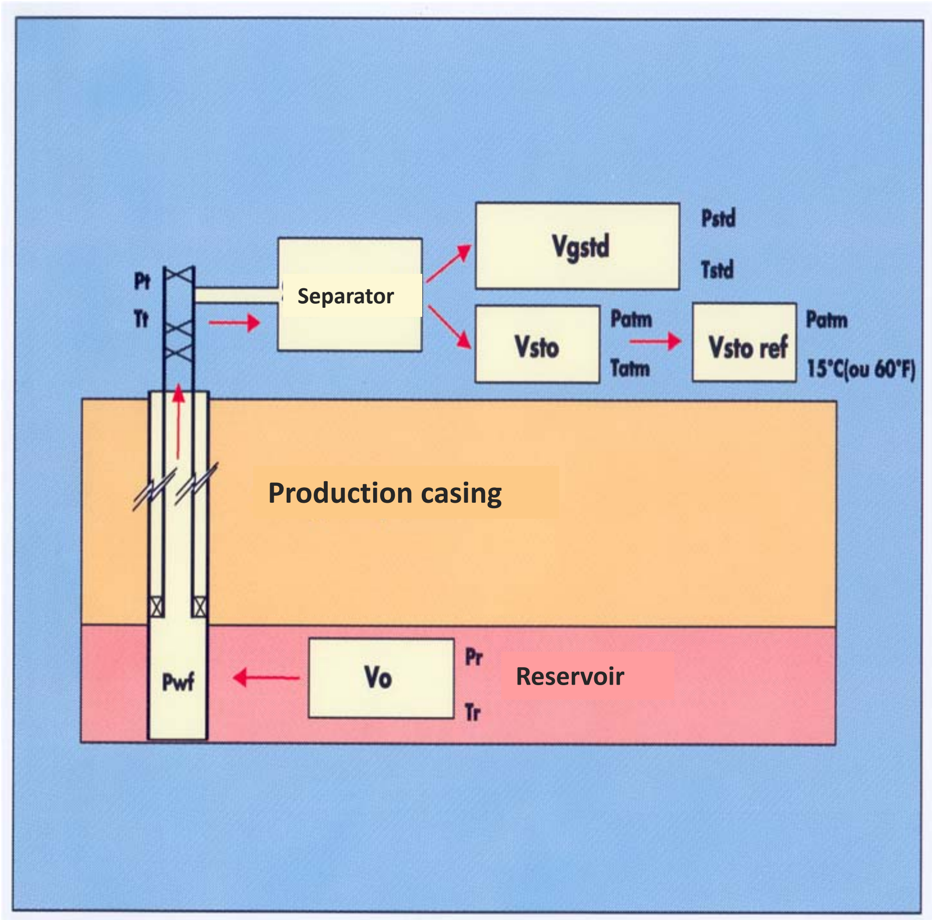
9. Calculation of OOIP/OGIP

Summary

Black-oil data

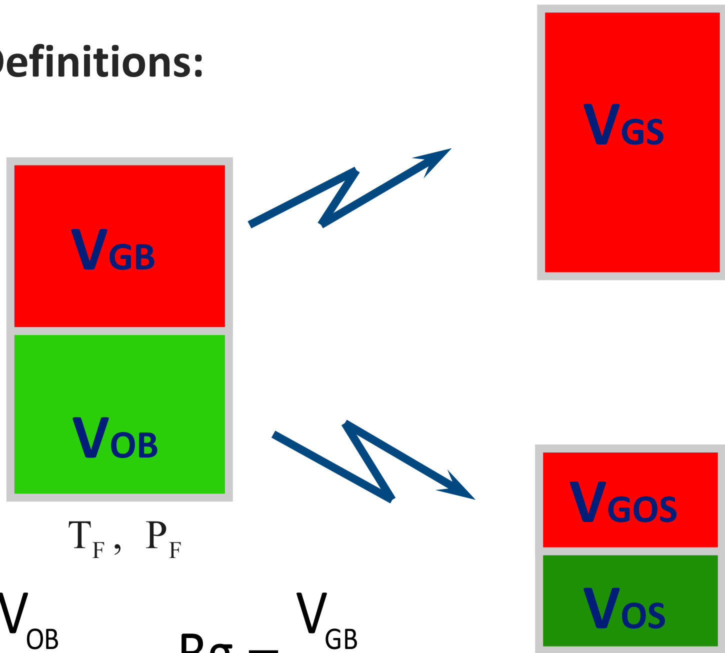
Summary

Black-Oil model



Black-Oil model

Definitions:



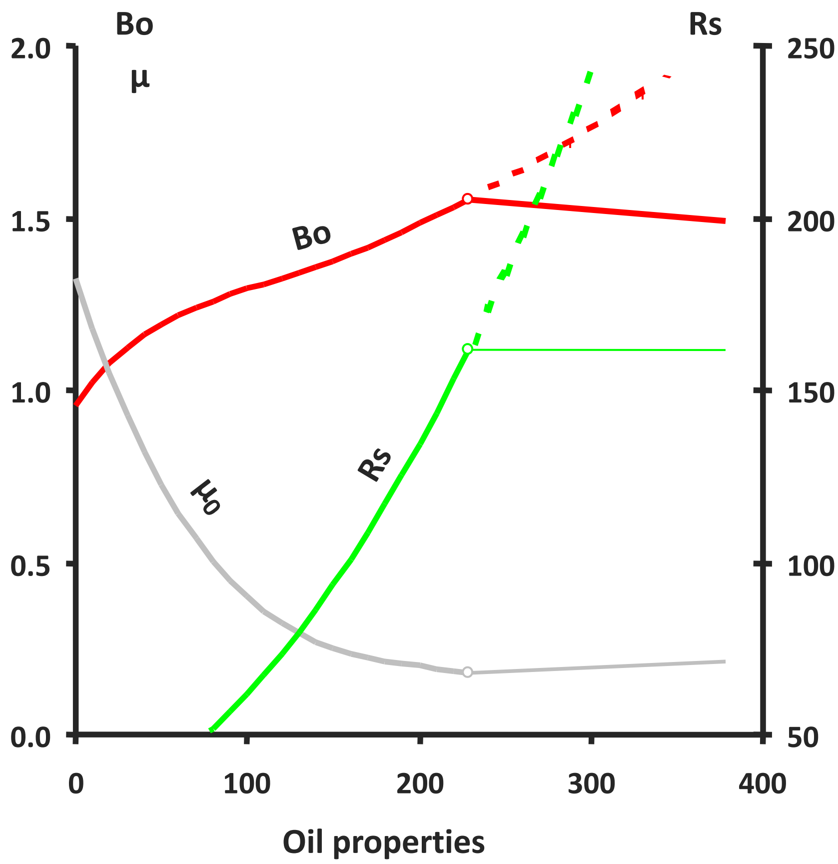
T_F , P_F

T_s , P_s

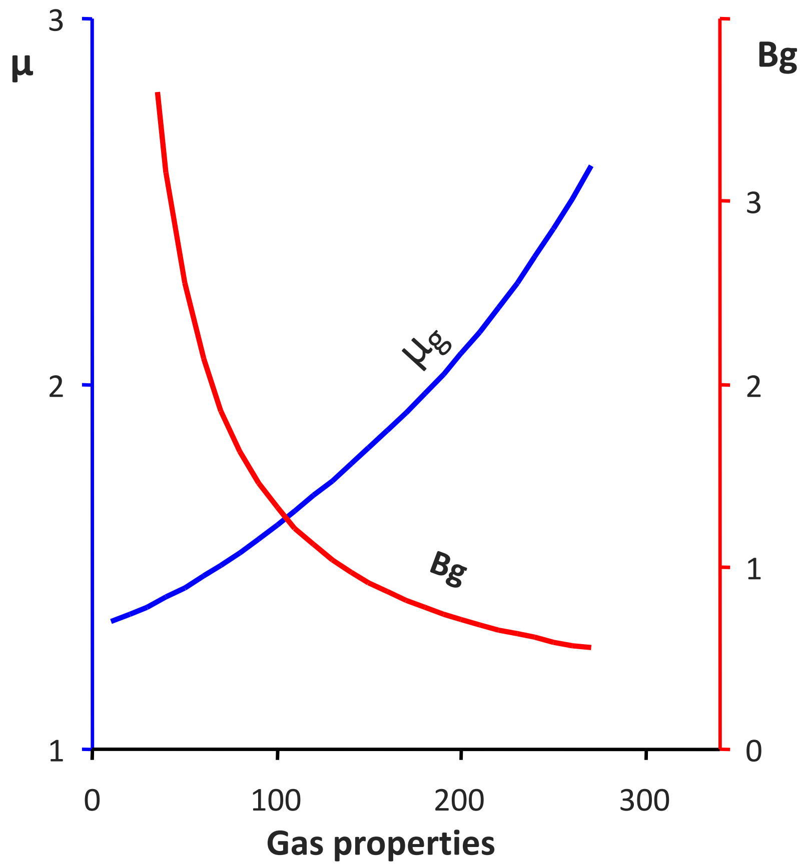
$$Bo = \frac{V_{OB}}{V_{OS}} \qquad Bg = \frac{V_{GB}}{V_{GS}}$$

$$Rs = \frac{V_{GOS}}{V_{OS}}$$

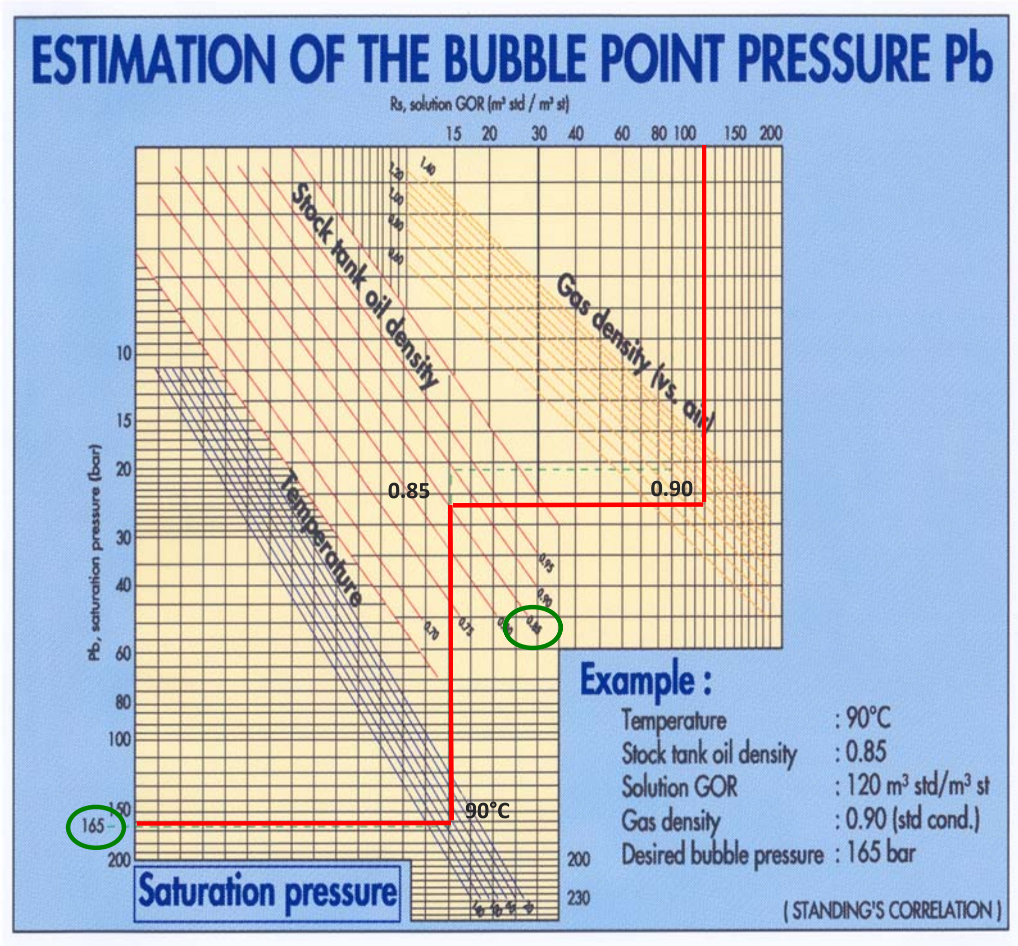
Black-Oil model



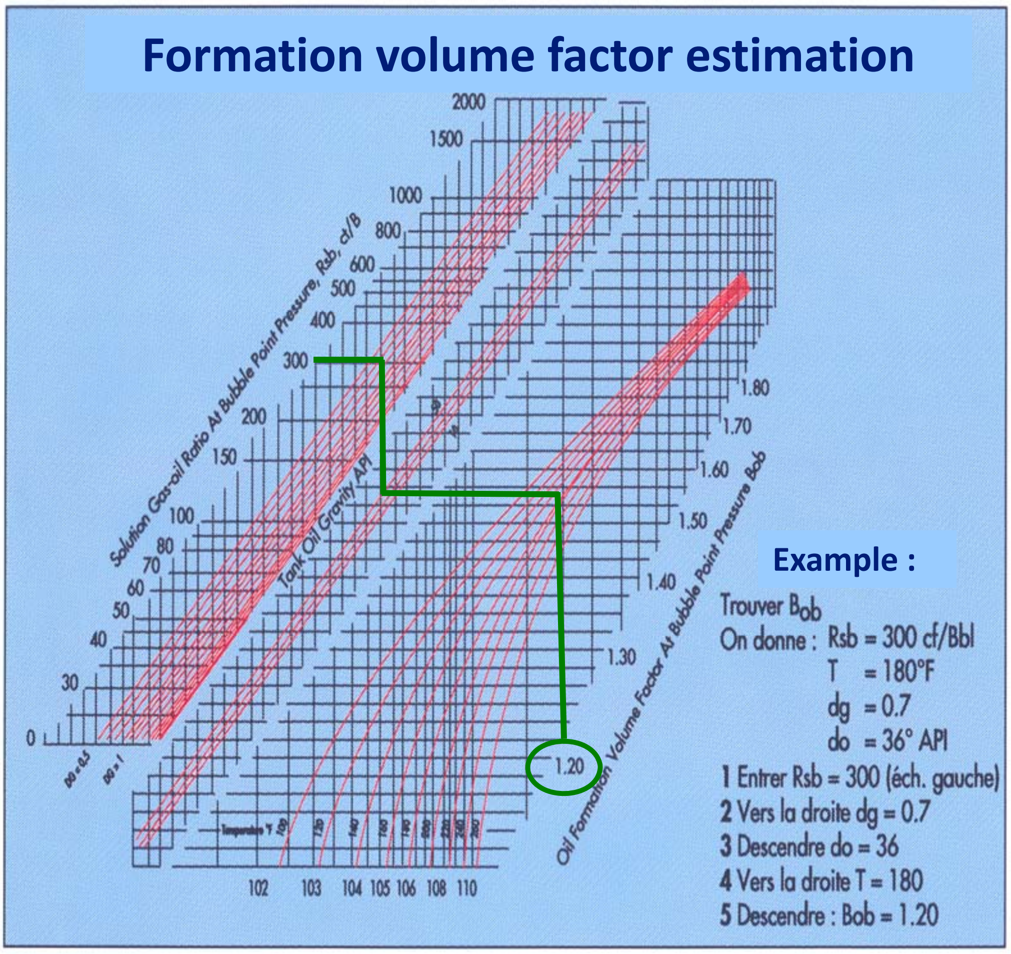
Black-Oil model



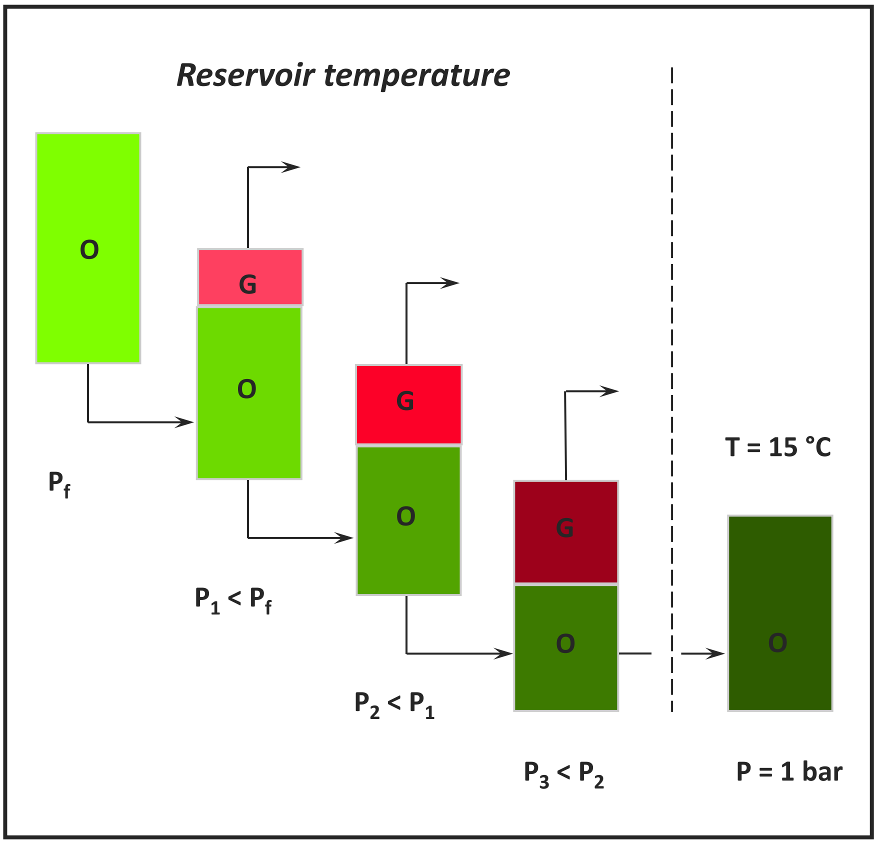
Black-Oil: correlations



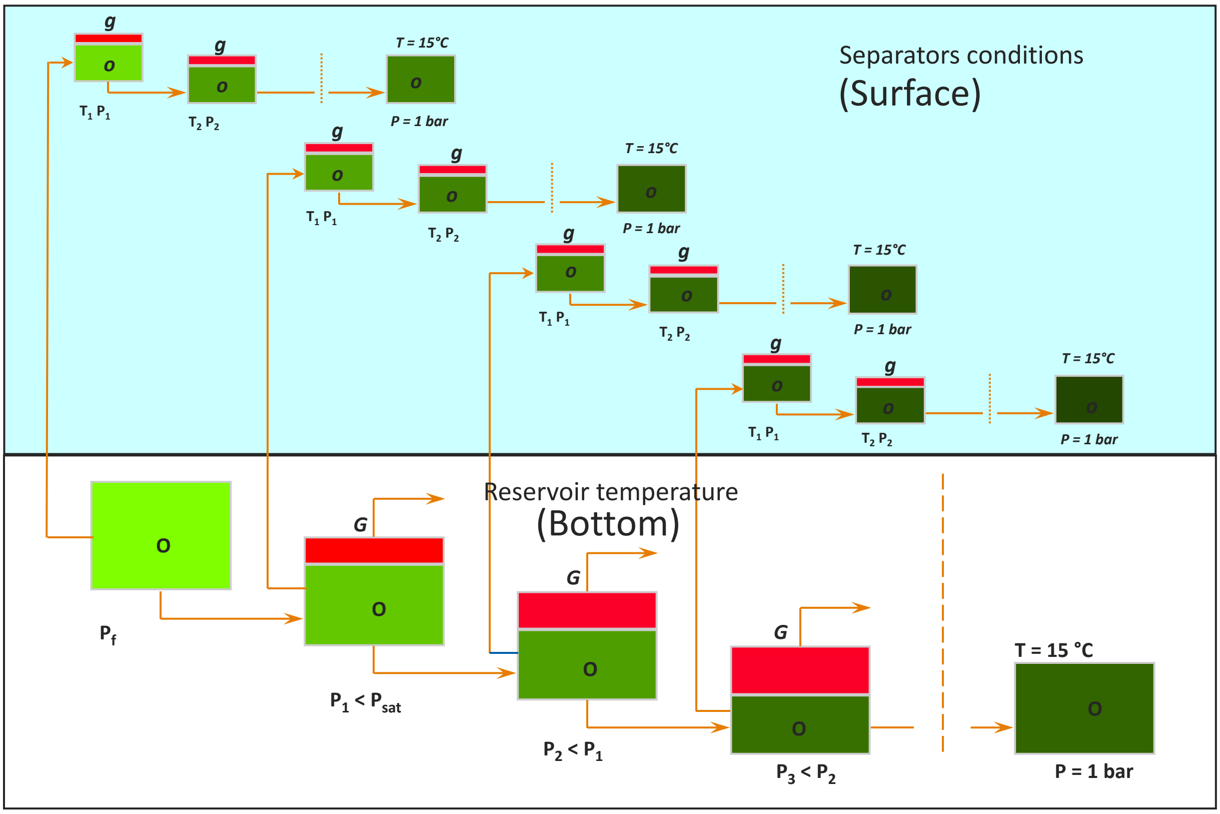
Black-Oil: correlations



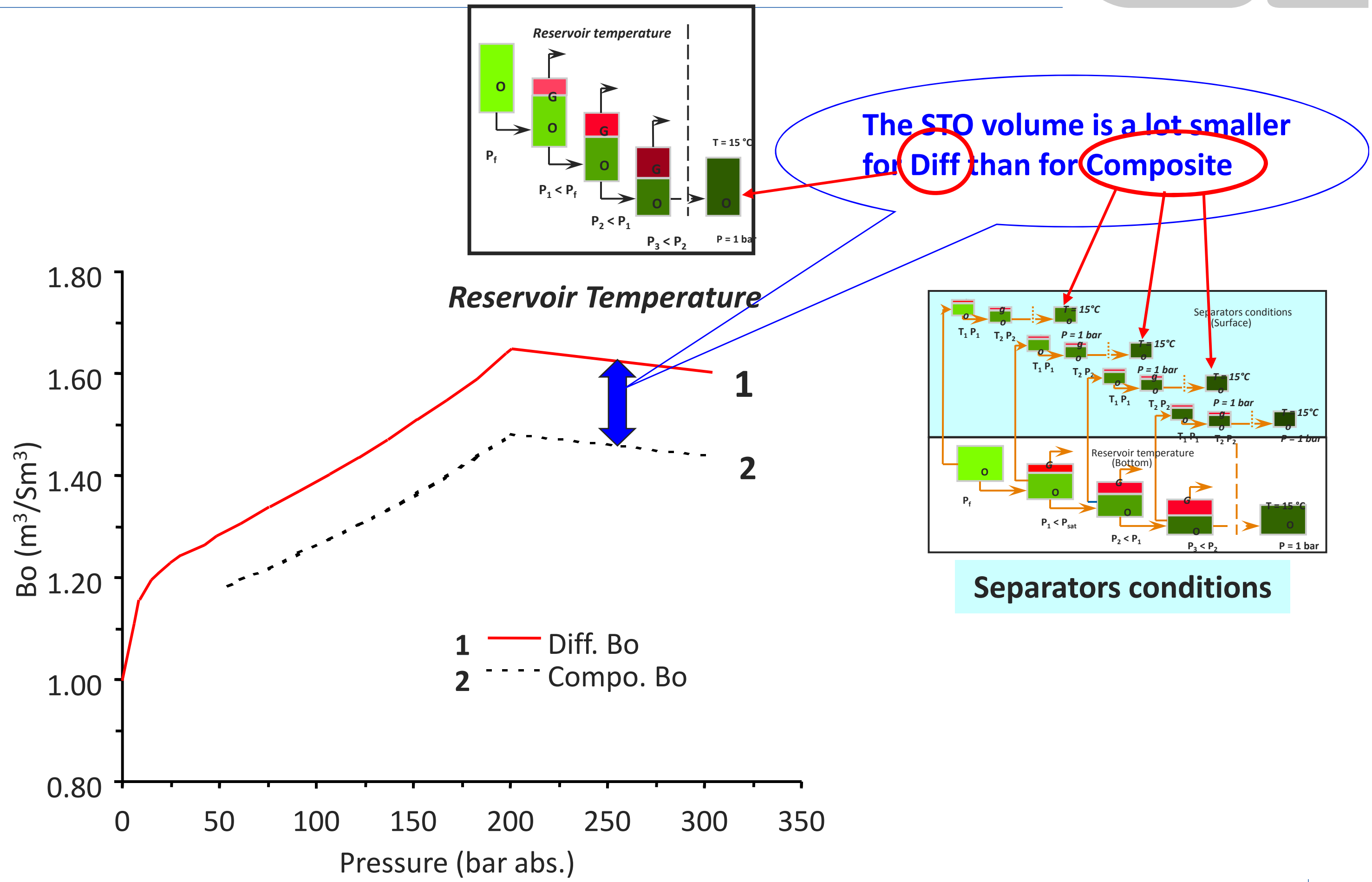
Differential vaporisation



Composite Bo

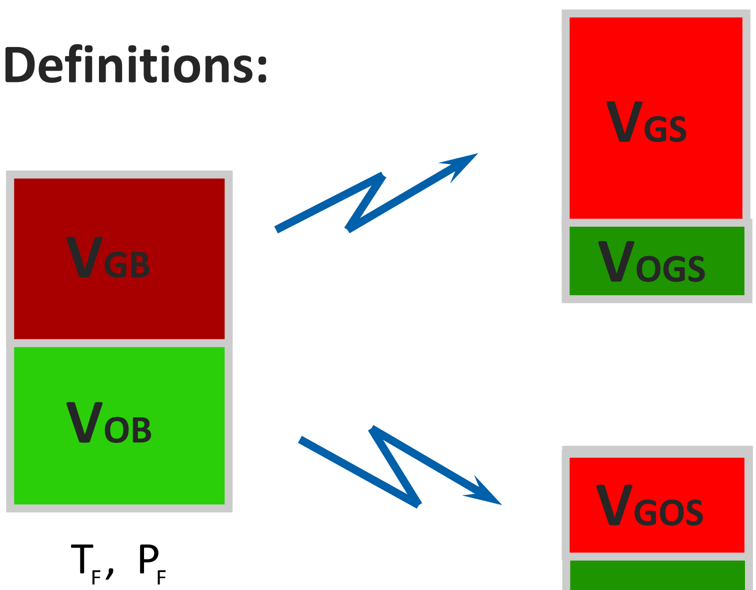


Comparison of Bo



Extended Black-Oil model

Definitions:

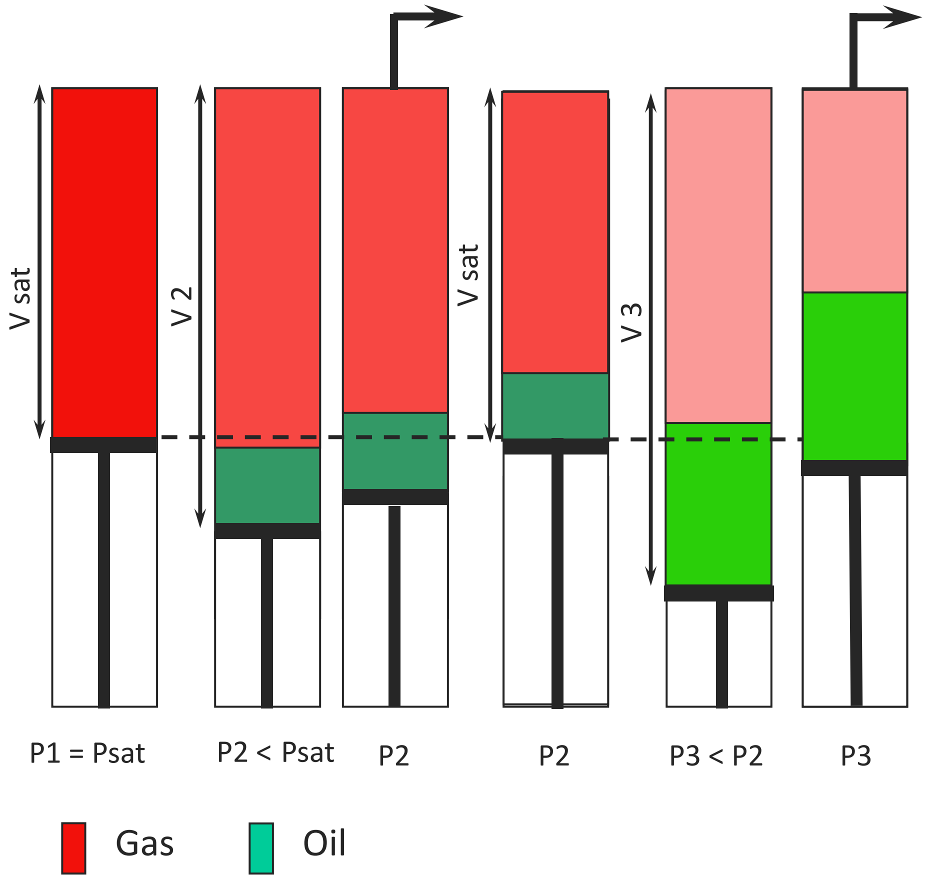


T_F, P_F $\qquad$ T_S, P_S

$$Bo = \frac{V_{OB}}{V_{OS}} \qquad Bg' = \frac{V_{GB}}{V_{GS}}$$

$$Rs = \frac{V_{GOS}}{V_{OS}} \qquad Rv = \frac{V_{OGS}}{V_{GS}}$$

Constant volume gas depletion

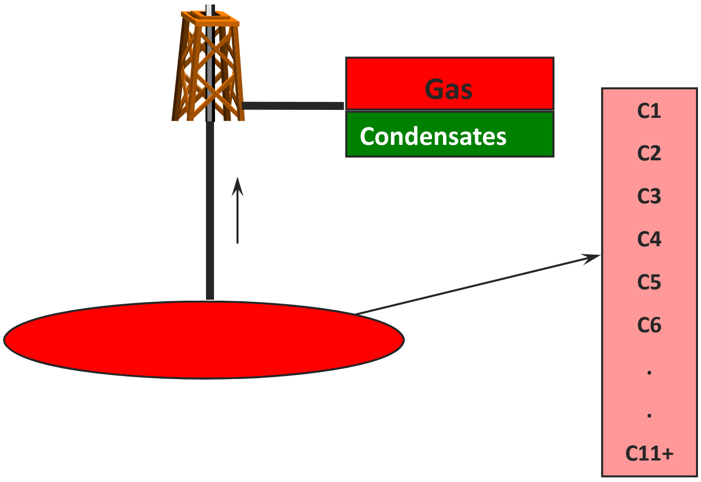


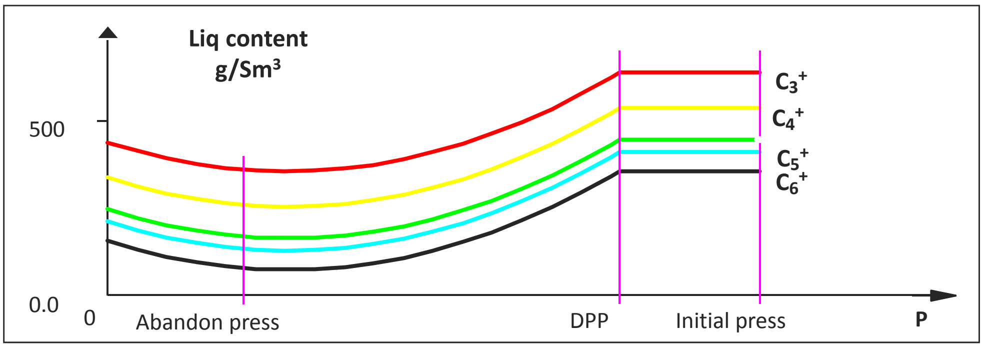
Black-oil quantities

WARNING!!

- **For an oil:**
  - Bo(P) and Rs(P) depend on the process
- **For a gas:**
  - Bg(P) is independent of the process
- **For a condensate / wet gas:**
  - Rv(P) and Bg'(P) depend on the process

Condensate content





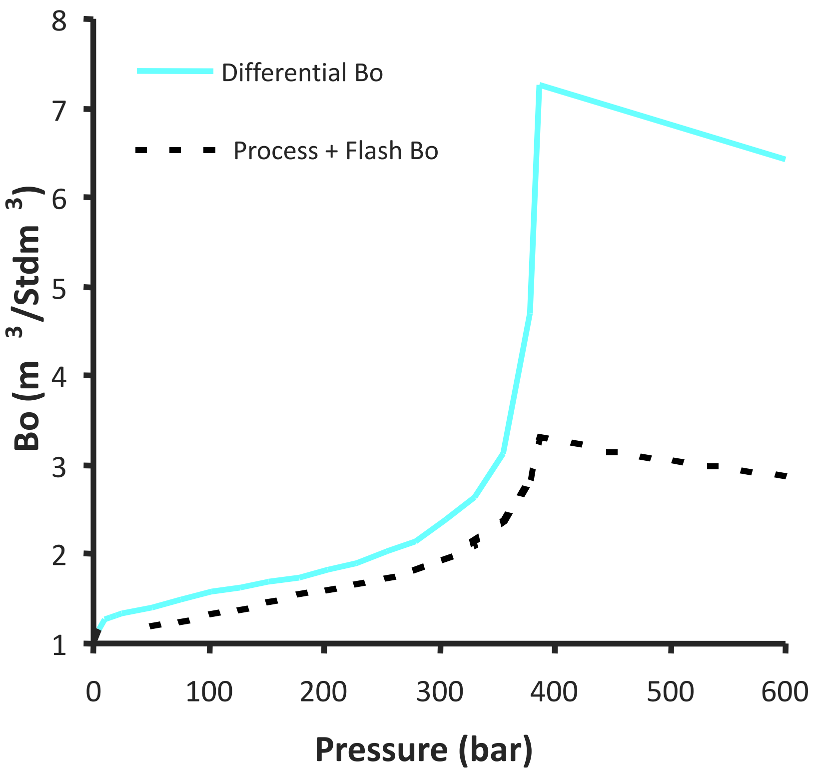
Composite black-oil quantities

- **From a PVT study:**
  - process test
  - differential liberation

1. **P > P sat**
   - Boc (P) = V(P) / V(Psat) * Bop (Psat)
   - Rsc (P) = Rsp (Psat)

2. **P < P sat**
   - Boc (P) = Bod (P) * (Bop (Psat) / Bod (Psat))
   - Rsc (P) = Rsp (Psat) - ΔRsd(P) * (Bop (Psat)/Bod (Psat))
   - ΔRsd(P) = Rsd (Psat) - Rsd (P)

Bo for a volatile oil



Compositional data

Summary

Compositional data: characterization of cuts

COMPOSITION AND PHYSICAL PROPERTIES							
Name	ZF %	Mw	Tc (K)	Pc (bar)	Acent fact	Vc (cm3)	Parachor
GN1	71.61	16.12	190.31	45.88	0.0116	98.9	76.6995
GN2	11.19	31.28	301.25	49.65	0.0957	143.0	105.4330
GN3	7.11	48.95	387.44	40.49	0.1600	221.5	162.1903
GN4	3.87	84.05	506.62	32.49	0.2621	351.9	268.0716
GN5	2.27	122.66	618.15	26.34	0.3000	511.8	422.4642
GN6	3.11	204.81	702.45	18.50	0.6000	975.0	481.6625
GN7	0.84	340.00	787.25	17.50	0.9200	1320.0	799.5959

BINARY INTERACTION COEFFICIENTS							
	GN1	GN2	GN3	GN4	GN5	GN6	GN7
GN1		-0.00155	0.00032	0.00890	0.01851	0.05840	0.06738
GN2	-0.00155		0.00840	0.00137	0.00278	0.04802	0.04800
GN3	0.00032	0.00840		0.00146	0.00276	0.02998	0.02999
GN4	0.00890	0.00137	0.00146		0	0	0
GN5	0.01851	0.00278	0.00276	0		0	0
GN6	0.05840	0.04802	0.02998	0	0		0
GN7	0.06738	0.04800	0.02999	0	0	0	

Why lumping?

- Because of the high number of components, the analysis of a large PVT report may reveal impractical on a small or overloaded machine
- The cost of EOS calculations are directly related to the number of components (N_c^2) used to characterize the reservoir fluid studied.
- In reservoir simulation of the compositional type, the EOS calculations must be repeated numerously in each grid block and at each time step. (reducing the number of components → reducing the number of equations)
- For anything but the simplest (or economically limited) reservoir cases, a complete compositional simulation using an extended fluid analysis becomes prohibitive in time and cost terms.
- What is required is a procedure, which will maintain the thermodynamic consistency while using a minimum number of representative components or 'pseudo-components'.

How to lump

According to the constraints due to

1. **Simulation:**
   - Kind of fluid
   - Production scheme (gas injection …)
   - Thermodynamic phenomena
2. **Process:**
   - Surface treatment (particularly for the gas phase)
   - Specifications

Rules for grouping

- **K values with the same magnitude**
  - C_1 - N_2
  - C_2 - CO_2 - C_3
  - C_4 - C_5
  - C_6 - C_{10} < C_6 - C_7 / C_8 - C_{10}
  - $C_{11}P$
- **Similarity of properties**
- **Insensitivity of experiments to trial grouping**
- **Example:**
  - Obvious candidates
  - iC_4 and $nC_4 \rightarrow C_4$
  - iC_5 and $nC_5 \rightarrow C_5$

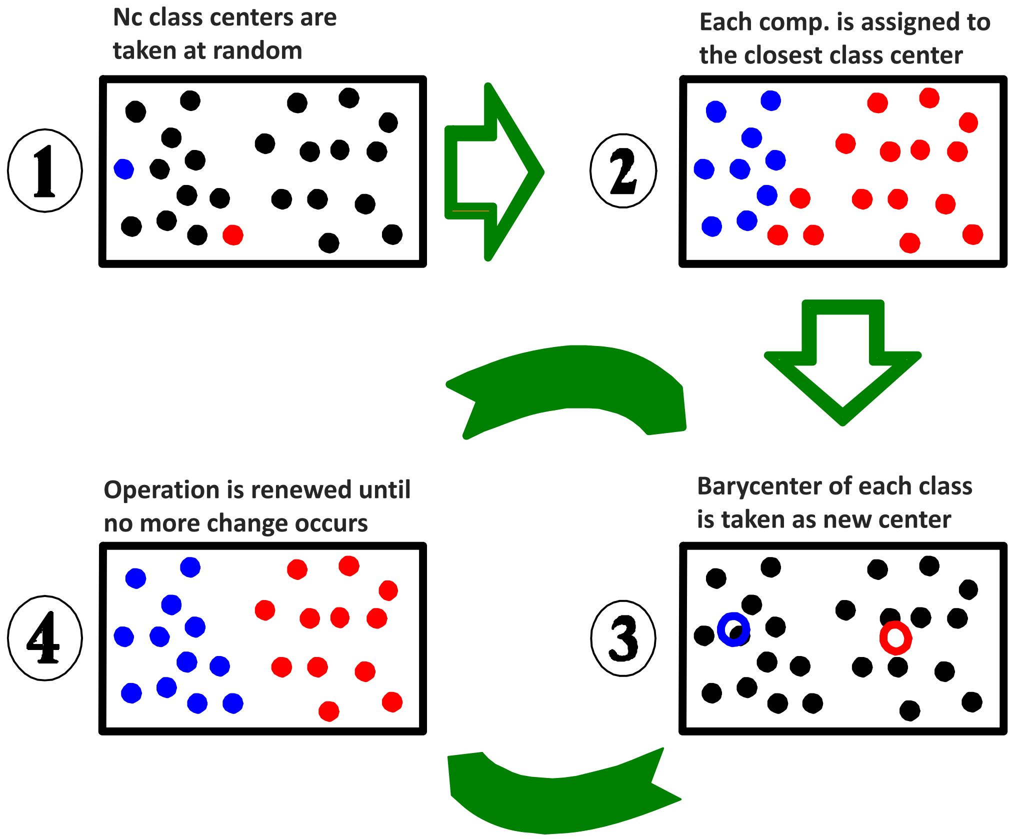
- **Lumping scheme (SPE 13119)**
  - Properties chosen

$$\sqrt{a_i} = \frac{\sqrt{0.45724}\, R\, T_{Ci}}{\sqrt{P_{Ci}}}$$

$$b_i = \frac{0.0778\, R\, T_{Ci}}{P_{Ci}}$$

$$m_i = f(\omega_i) \text{ and } M_i$$

Lumping algorithm



Properties calculation

$$T_C = \frac{\displaystyle\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{Z_i Z_j T_{C_i} T_{C_j}}{\sqrt{P_{C_i} P_{C_j}}}}{\displaystyle\sum_{i=1}^{n}\frac{Z_i T_{C_i}}{P_{C_i}}}$$

$$k_{nm} = \frac{\displaystyle\sum_{i=L_n}^{U_n}\sum_{j=L_m}^{U_m} z_i z_j M_i M_j k_{ij}}{\overline{M}_n \overline{M}_n \displaystyle\sum_{i=L_n}^{U_n} z_i \sum_{j=L_m}^{U_m} z_j}$$

$$P_C = \frac{T_C}{\displaystyle\sum_{i=1}^{n}\frac{Z_i T_{C_i}}{P_{C_i}}}$$

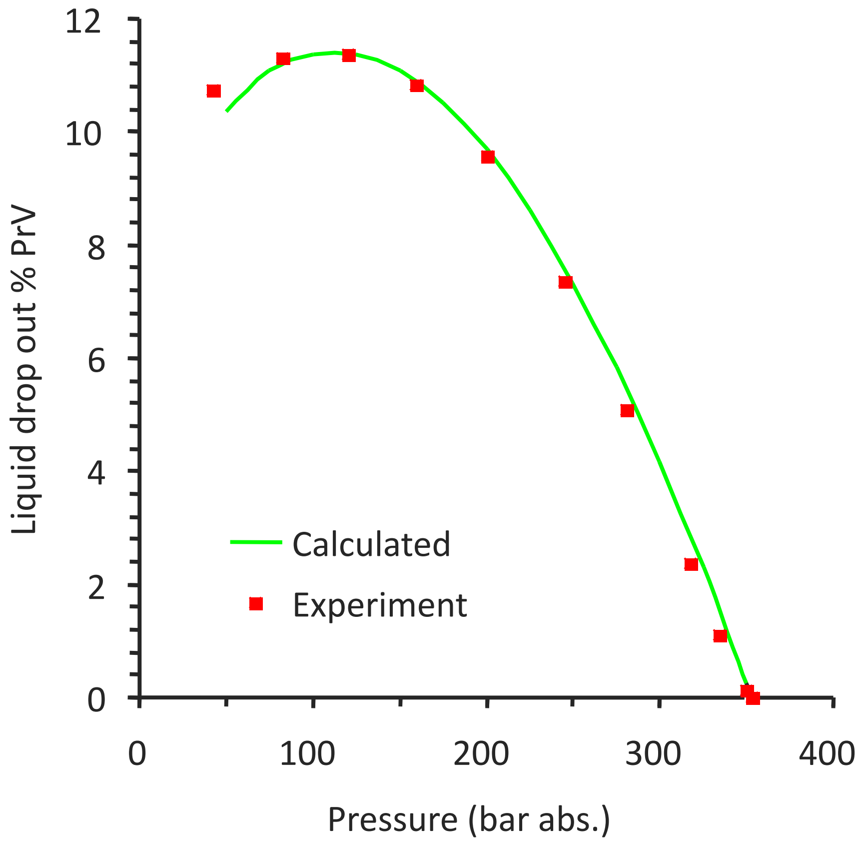
$$\omega = \sum_{i=1}^{n} Z_i \omega_i$$

$$M = \sum_{i=1}^{n} X_i \cdot M_i$$

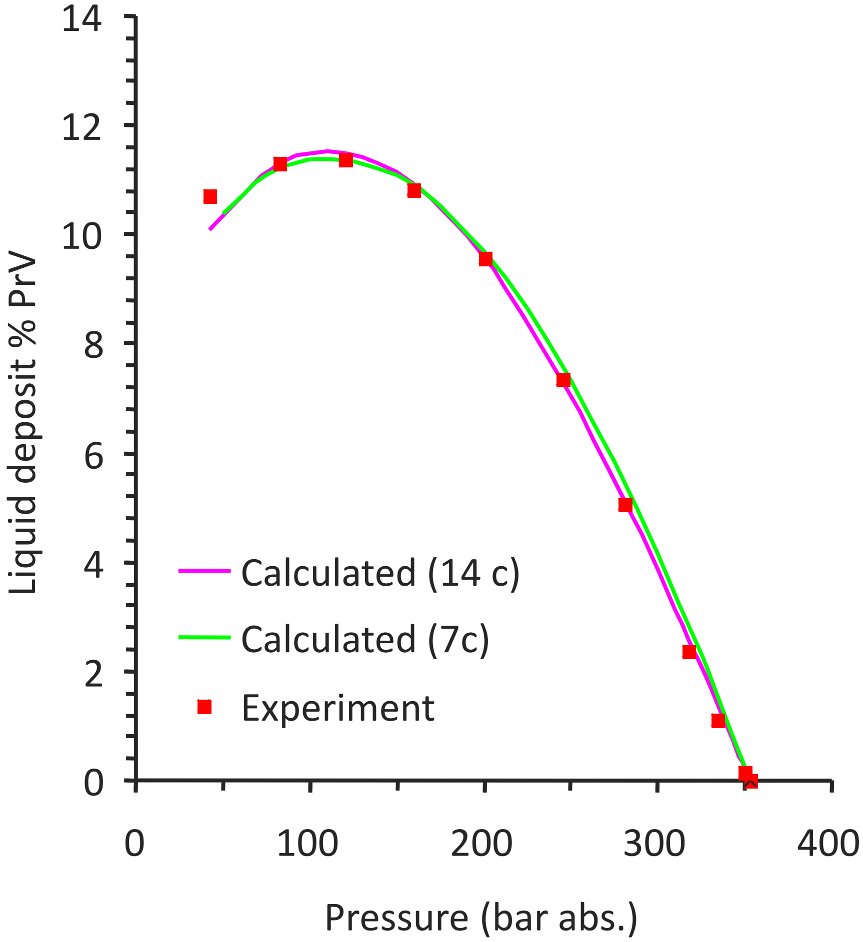
Results of a 7-component match

	Valeurs mesurées	Valeurs simulées	Erreur relative %
$P_{rosée}$	353.000	353.000	0.00
ρ_V à P_{sat}	0.315	0.314	0.32
ρ_V à P_{fond}	0.312	0.312	0.00
GOR sep	1631.800	1783.837	9.31
ρ_L sep	0.722	0.734	1.66
ρ_L Std	0.779	0.786	0.90
Simulation du dépôt liquide			
Pression bar abs	Valeurs mesurées	Valeurs simulées	
353.0	0.000	0.000	
350.0	0.135	0.259	Voir figure
334.5	1.111	1.553	
318.0	2.368	2.847	
281.0	5.075	5.459	
245.5	7.359	7.585	
201.0	9.574	9.654	
159.0	10.824	10.899	
120.0	11.360	11.381	
82.0	11.313	11.186	
42.0	10.722	10.008	

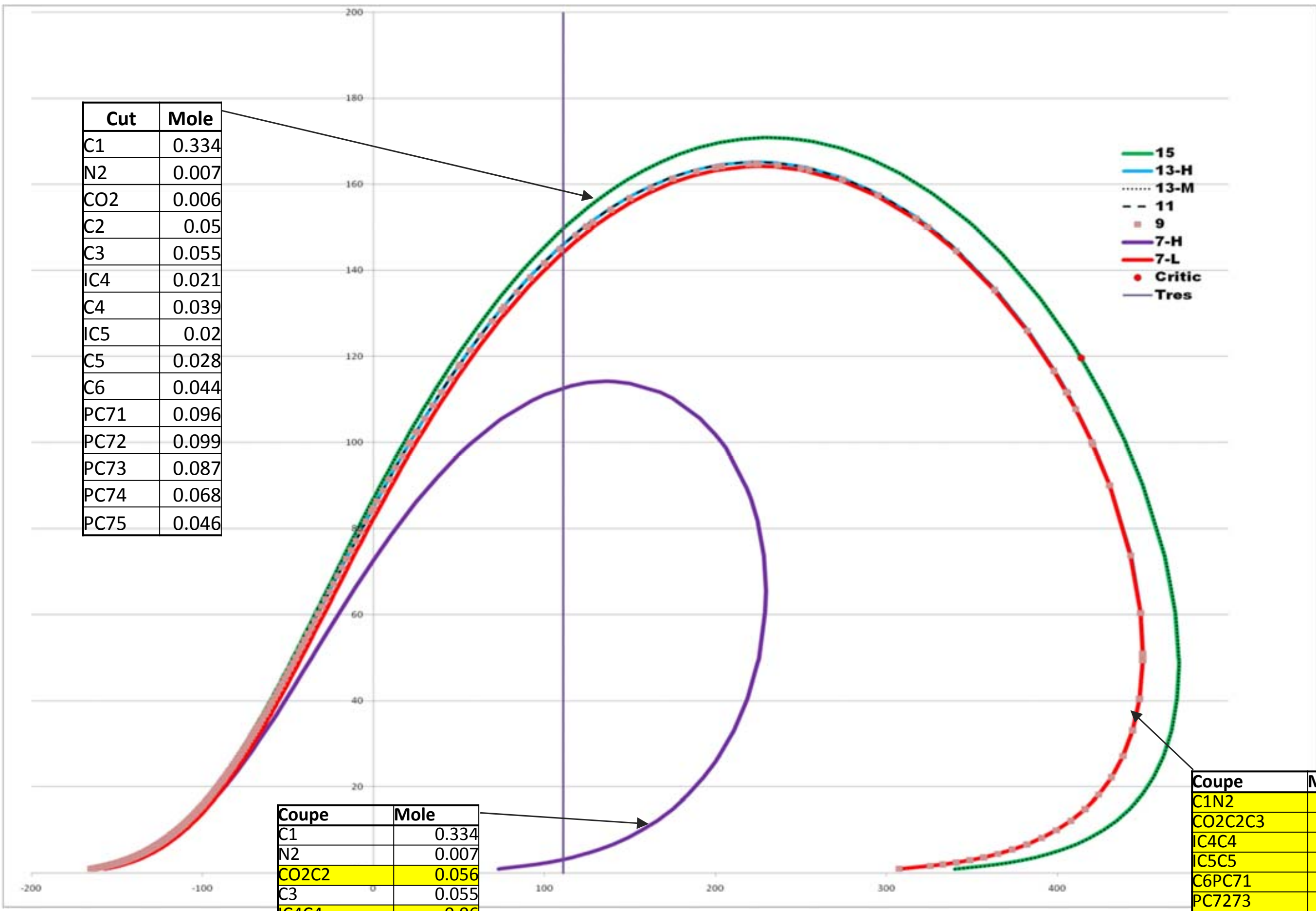
Results of a 7-component match



Results of a 14 and a 7-component match



Results for different groupings



Cut	Mole
C1	0.334
N2	0.007
CO2	0.006
C2	0.05
C3	0.055
IC4	0.021
C4	0.039
IC5	0.02
C5	0.028
C6	0.044
PC71	0.096
PC72	0.099
PC73	0.087
PC74	0.068
PC75	0.046

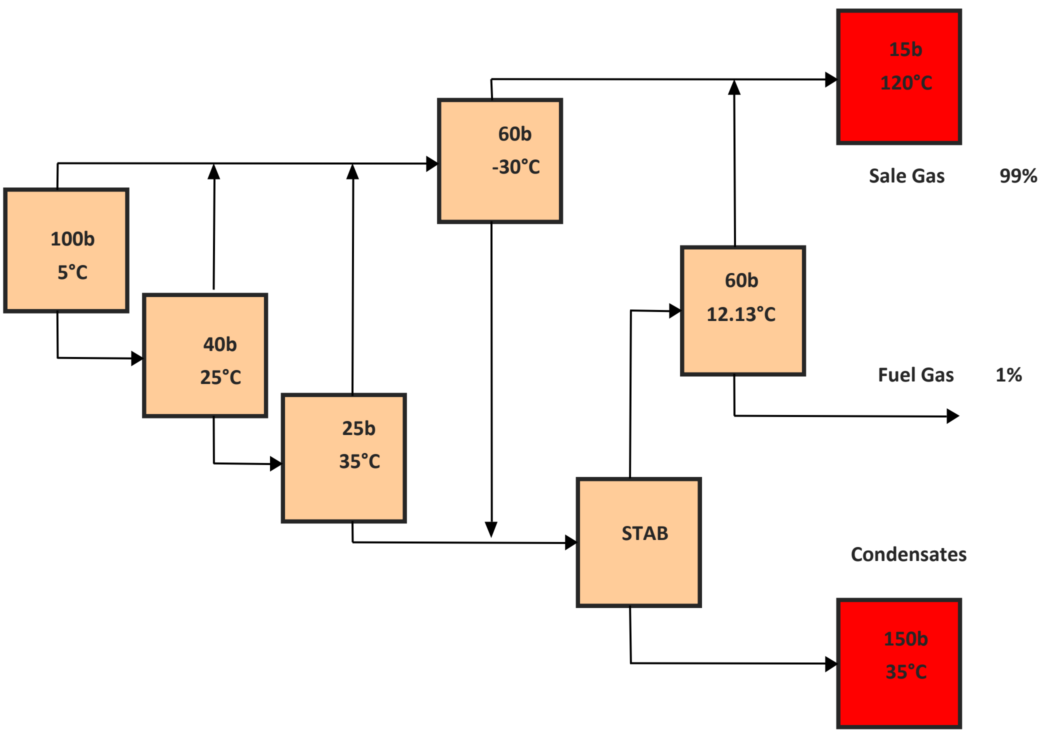
Coupe	Mole
C1	0.334
N2	0.007
CO2C2	0.056
C3	0.055
IC4C4	0.06
IC5C5	0.048
C6P	0.44

Coupe	Mole
C1N2	0.341
CO2C2C3	0.111
IC4C4	0.06
IC5C5	0.048
C6PC71	0.14
PC7273	0.186
PC7475	0.114

Properties profile vs depth

N°	Cote en m/TR	P.fond bar abs.	T. fond °C	Vis. fond cPo	ρ fond Kg/m^3	P. sat bar abs.	Vis. sat cPo	ρ sat Kg/m^3	Rs m^3/m^3	Bo m^3/m^3	ρ std Kg/m^3
1	-3040.0	390.30	136.30	0.0420	320.10	352.48	0.0398	302.50	2053.38	8.1135	779.3
2	-3060.0	390.90	136.80	0.0426	323.00	356.06	0.0404	306.90	1976.57	7.8420	780.1
3	-3080.0	391.60	137.30	0.0431	325.80	358.02	0.0411	310.40	1903.34	7.5692	780.1
4	-3100.0	392.20	137.80	0.0437	328.90	361.03	0.0422	314.80	1830.09	7.3038	780.6
5	-3125.8	393.10	138.40	0.0446	333.50	364.57	0.0435	320.70	1732.10	6.9467	781.1
6	-3151.6	393.90	139.10	0.0457	338.80	368.53	0.0450	327.50	1629.21	6.5746	781.8
7	-3177.4	394.80	139.70	0.0470	345.00	372.72	0.0472	335.20	1523.92	6.1910	782.6
8	-3203.2	395.70	140.40	0.0488	353.10	378.43	0.0502	345.60	1401.78	5.7477	784.0
9	-3229.0	396.60	141.00	0.0515	364.10	384.18	0.0519	358.80	1261.60	5.2380	785.4
10	-3239.2	396.96	141.25	0.0530	370.00	386.89	0.0542	365.80	1196.22	5.0008	786.2
11	-3249.4	397.33	141.51	0.0551	377.60	389.74	0.0580	374.40	1119.60	4.7238	787.1
12	-3259.6	397.70	141.80	0.0585	386.00	393.59	0.0990	387.40	1018.49	4.3588	788.7
13	-3269.8	398.10	142.02	0.0996	468.70	395.93	0.1142	467.90	582.81	2.8162	799.7
14	-3280.0	398.57	142.27	0.1165	486.80	391.67	0.1246	384.60	519.96	2.6020	802.5
15	-3290.2	399.06	142.53	0.1286	397.30	388.45	0.1334	493.90	487.17	2.4918	804.2
16	-3300.4	399.56	142.78	0.1389	505.10	386.00	0.1412	500.80	464.42	2.4159	805.6
17	-3310.6	400.06	143.04	0.1484	511.50	383.73	0.1484	506.40	446.53	2.3566	806.8
18	-3320.8	400.57	143.29	0.1574	517.00	381.62	0.1553	511.20	431.80	2.3081	807.8
19	-3331.0	401.09	143.55	0.1661	521.90	379.64	0.1615	515.40	419.05	2.2664	808.7
20	-3341.2	401.61	143.80	0.1742	526.10	377.81	0.1678	519.00	408.38	2.2316	809.5
21	-3351.4	402.14	144.06	0.1823	530.10	376.13	0.1742	522.40	398.64	2.2000	810.4
22	-3361.6	402.67	144.31	0.1907	533.90	374.60	0.1799	525.60	389.70	2.1710	811.2
23	-3371.8	403.20	144.57	0.1984	537.20	372.89	0.1855	528.40	381.67	2.1452	811.8
24	-3382.0	403.74	144.82	0.2062	540.40	371.40	0.1913	531.00	374.56	2.1224	812.5
25	-3392.2	404.28	145.08	0.2142	543.50	369.85	0.1971	533.60	367.46	2.0997	813.1
26	-3402.4	404.83	145.33	0.2223	546.40	368.54	0.2026	636.00	361.11	2.0793	813.8
27	-3412.6	405.37	145.59	0.2300	549.00	367.18	0.2081	538.20	355.25	2.0607	814.4
28	-3422.8	405.92	145.84	0.2380	551.70	365.79	0.2137	540.40	349.51	2.0425	814.9

Pseudo process



Pseudo process

- **Split factors are used in STAB to obtain a liquid without methane**

- **The following split factors are used to restore the composition of the condensate over several years,**
  - N2: 100%, CO2: 100%, C1: 100%,
  - C2: 96%, C3: 58%, iC4: 13%, nC4: 10%
  - iC5: 0, nC5: 0, …….

Lumping / ungrouping

Hypothesis : δ_{ij} are zero

$$\Phi_i^L = \mathrm{Ln}\,[f_i^L/(xi.P)] = C_0^L + C_1^L\,(a_i)^{1/2} + C_2^L\, b_i$$

$$\Phi_i^V = \mathrm{Ln}\,[f_i^V/(yi.P)] = C_0^V + C_1^V\,(a_i)^{1/2} + C_2^V\, b_i$$

At equilibrium : $f_i^L = f_i^V$

$$\mathrm{Ln}\,K_i = \mathrm{Ln}\,(y_i / x_i) = \Phi_i^L - \Phi_i^V$$

$$\mathrm{Ln}\,K_i = \Delta C_0 + \Delta C_1\,(a_i)^{1/2} + \Delta C_2\, b_i$$

$$\boxed{\mathrm{Ln}\,K_i = C_0 + C_1\,(a_i)^{1/2} + C_2\, b_i}$$

Fugacity

- **Fugacity coefficient of component k in a mixture (Peng-Robinson's EOS)**

$$\mathrm{Log}\left(\frac{f_k}{Px_k}\right)=\frac{b_k}{b_m}(Z-1)-\mathrm{Log}(Z-B)$$
$$-\frac{A}{2\sqrt{2}B}\left(\frac{2\sum_i^n x_i a_{ik}}{a_m}-\frac{b_k}{b_m}\right)$$
$$\times\mathrm{Log}\left(\frac{Z+2.414B}{Z-0.414B}\right)$$

with: $a_{ik}=\sqrt{a_i\cdot a_k}$

when: $\delta_{ik}=0$

Lumping / ungrouping

- **From:**
  - 7 pseudo-components (z_i) to 16 components (Z_i)
- **Equilibrium @ 7 pseudo-components:**
  - We know: x_i, y_i and Θ ➔ k_i
  - There are: 7 equations $Ln(k_i) = C_0 + C_1 (a_i)^{½} + C_2 b_i$ ➔ C_0, C_1 and C_2
- **Hypothesis:**
  - Θ is the same for the 2 representations (7 and 16 comp.).
  - For the 16 components we know: Z_i, Θ, C_0, C1 and C_2 so Z_i, Θ and K_i

$$X_i = Z_i / (1 + \Theta (K_i - 1))$$
$$Y_i = Z_i K_i / (1 + \Theta (K_i - 1))$$

Lumping / ungrouping

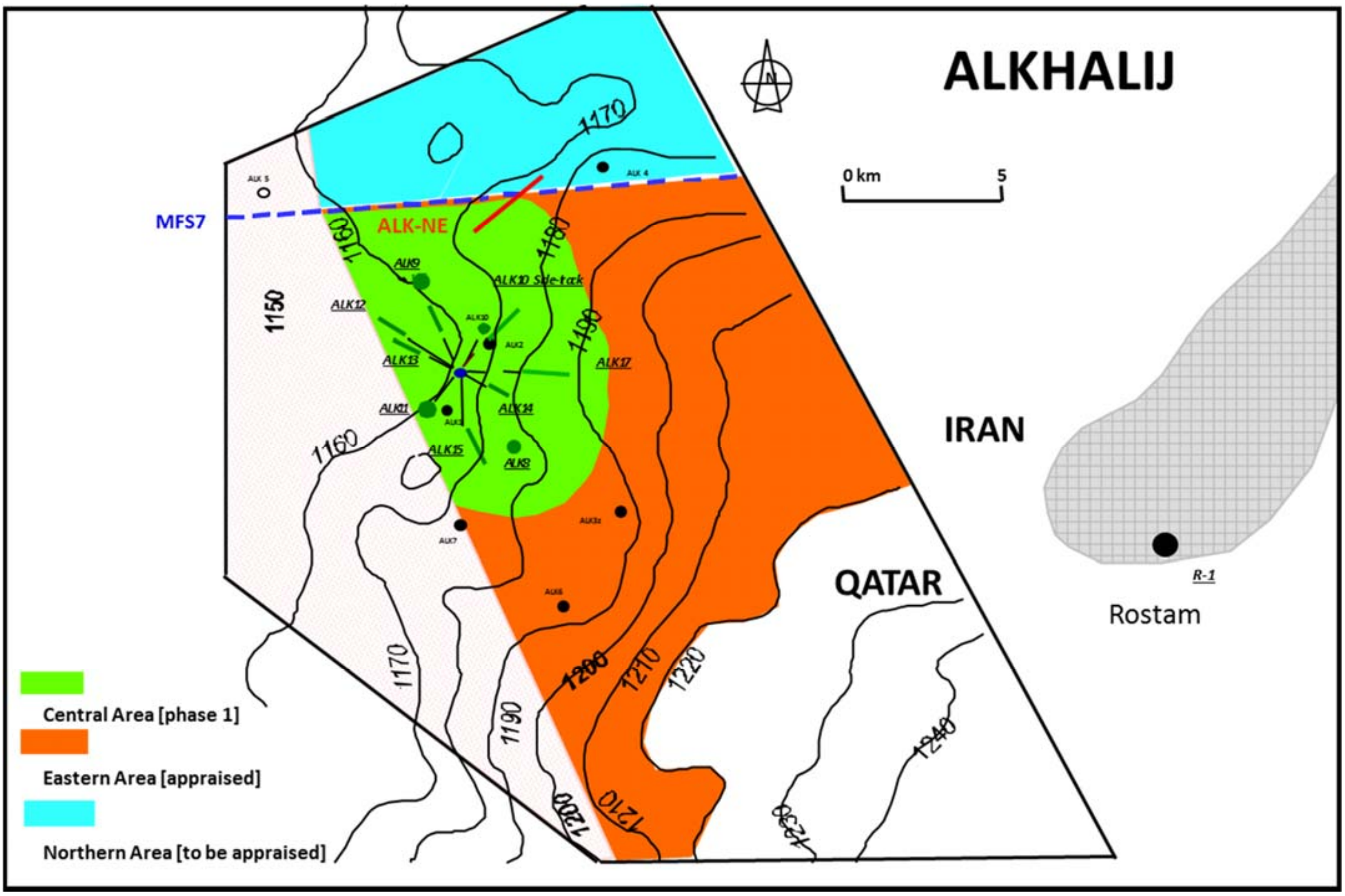
- For a condensate gas, a CVD can be numerically performed with a detailed fluid representation.

- So, the detailed compositional profile of the produced gas versus the reservoir pressure is obtained.

- At a given reservoir pressure, each pseudo component is ungrouped according to the new “true” proportions.

Fluid synthesis

Field case / A



Field case / A

Properties	Initial A3 DST1 1992	A NE MDT 2000
BH conditions		
(52.7°C - 131.7b)		
Density (kg/m3)	822,3	**833,6**
Viscosity (cPo)	2,39	**4,27**
Saturation pressure (bar)	65,4	**32,6**
Density (kg/m3)	814,6	**826,9**
Viscosity (cPo)	2,12	**3,48**
Process test		
(40°C-6.7b / 40°C-1b / 15°C-1b)		
Total GOR	43,2	
Boi	1,1218	
Liquid density (kg/m3) @ 40°C	862,1	
Stock tank liquid density (kg/m3)	874,3	
Composition test		
(50°C-1b / 15°C-1b)		
Total GOR		**20,1**
Boi		**1,1018**
Liquid density (kg/m3) @ 50°C		**868,8**
Stock tank liquid density (kg/m3)		**891**

Components	Initial A3 DST1 1992	A NE MDT 2000
N2	0,23%	**0,12%**
CO2	0,67%	**0,16%**
C1	17,74%	**6,91%**
C2	4,48%	**3,49%**
C3	4,98%	**4,65%**
IC4	1,24%	**1,27%**
NC4	3,27%	**3,40%**
IC5	1,97%	**2,26%**
NC5	2,18%	**2,48%**
C6	4,47%	**5,35%**
C7	4,30%	**5,57%**
C8	4,03%	**5,05%**
C9	3,68%	**4,97%**
C10	3,59%	**4,63%**
C11P	43,17%	**49,69%**

Field case / A

2 wells: A3 and A-NE

**Very different compositions,
very different PVT behaviors,
about 10km apart with a
possible sealing fault between them**

?

**2 different fluids:
compartmentalization**

Field case / A

Data from drilling

Problems during drilling,
the well has remained "under water" for 2 months

?

2 different fluids: compartmentalization

Washing by the mud filtrate

Field case / A

Geochemistry study

same origin,
same maturity,
no biodegradation

?

Washing by the mud filtrate

Thermodynamic study

fluid model for A3,
simulation of a multi-contact experiment
between A3 fluid and water

Soreide & Withson EOS

Properties	Initial A3 DST1 1992	After water washing (34 vol)	A NE MDT 2000
BH conditions			
(52.7°C - 131.7b)			
Density (kg/m3)	822,3	*844,8*	833,6
Viscosity (cPo)	2,39	*3,08*	4,27
Saturation pressure (bar)	65,4	*24,0*	32,6
Density (kg/m3)	814,6	*833,9*	826,9
Viscosity (cPo)	2,12	*2,60*	3,48
Process test			
(40°C-6.7b / 40°C-1b / 15°C-1b)			
Total GOR	43,2	*20,2*	
Boi	1,1218	*1,0668*	
Liquid density (kg/m3) @ 40°C	862,1	*861,2*	
Stock tank liquid density (kg/m3)	874,3	*873,5*	
Composition test			
(50°C-1b / 15°C-1b)			
Total GOR		*25,4*	20,1
Boi		*1,0890*	1,1018
Liquid density (kg/m3) @ 50°C		*861,3*	868,8
Stock tank liquid density (kg/m3)		*878,3*	891

Components	After water washing (34 vol)	A NE MDT 2000
N2	*0,05%*	0,12%
CO2	*0,00%*	0,16%
C1	*6,87%*	6,91%
C2	*3,54%*	3,49%
C3	*5,31%*	4,65%
IC4	*1,44%*	1,27%
NC4	*3,74%*	3,40%
IC5	*2,29%*	2,26%
NC5	*2,55%*	2,48%
C6	*5,22%*	5,35%
C7	*5,03%*	5,57%
C8	*4,72%*	5,05%
C9	*4,31%*	4,97%
C10	*4,21%*	4,63%
C11P	*50,59%*	49,69%

Field case / A

From MDT measurement, a slight trend can be observed on C1 content, the saturation pressure and GOR as a function of the pumping duration before sampling

MDT number	Pumping duration	C1 content (mol %)	BH density (kg/m3)	Sat. Press. (abs. bar)	GOR (Sm3/Sm3)	ST liq. Dens. (kg/m3)	Water content
90	**2h 30**	6,5	837,2	30,4	19,7	891	50%
128	**3h**	6,9	833,6	32,6	20,1	891	37,50%
129	**3h**	7,2	833,7	32,9	20,1	894,1	40%

No conclusion was drawn from this single trend

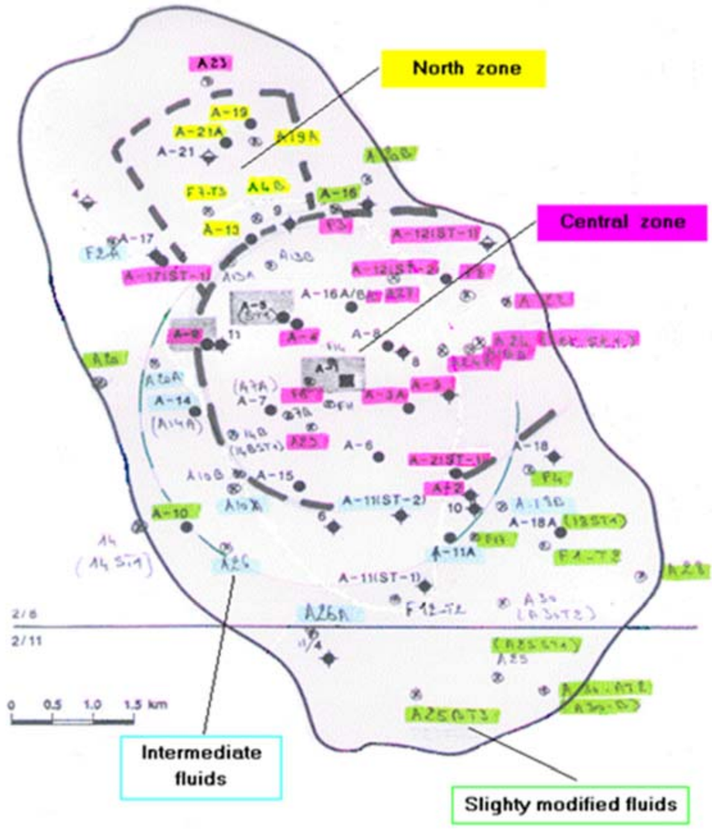
Field case / A

Conclusions

- **The unexpected A-NE sample composition can be explained by a water washing process**
- **A representative sample was obtained after a longer pumping period duration**

Later, the production data confirmed that the two fluids were identical (no compartmentalization)

Field case / V



Field case / V

- GOR measurements obtained from a lot of wells do not show any obvious trend according to perf depth and/or well location
- Highly undersaturated, the fluid exhibits a non classical GOR profile vs. depth: from 280 to 150 for only 70 m depth variation!

?

Different fluids: compartmentalization

Data from Geology – Geochemistry

2D Témis simulation on the Central Graben:
accumulation conditions (P, T)
(at the beginning (15 M years), saturated fluid with a gas-cap)

Sedimentation speeding up during the last 5 M years

?

Paleo gas-cap dissolution

Data from Geology – Geochemistry

Accumulation pressure # 250 b

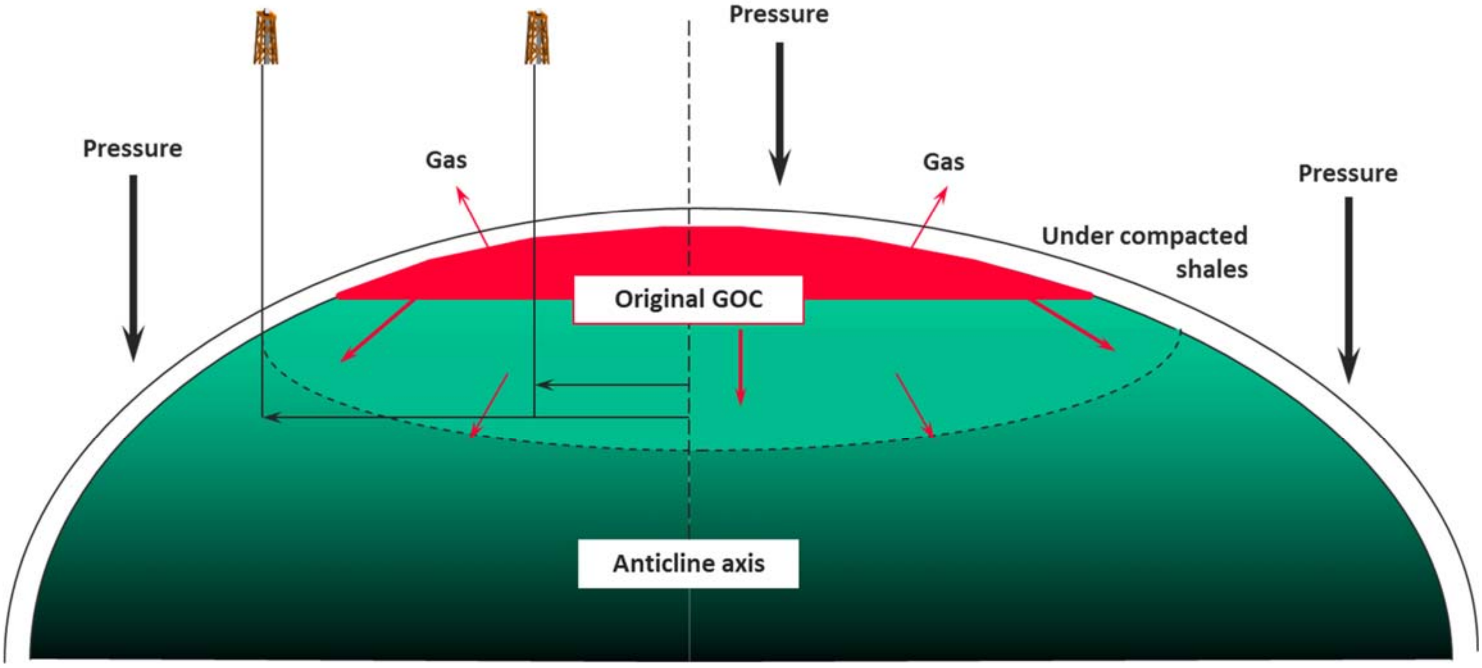
Data from Seismic

Due to a gas "cloud" over the cap-rock
It was difficult to interpret seismic data

Data from PVT study

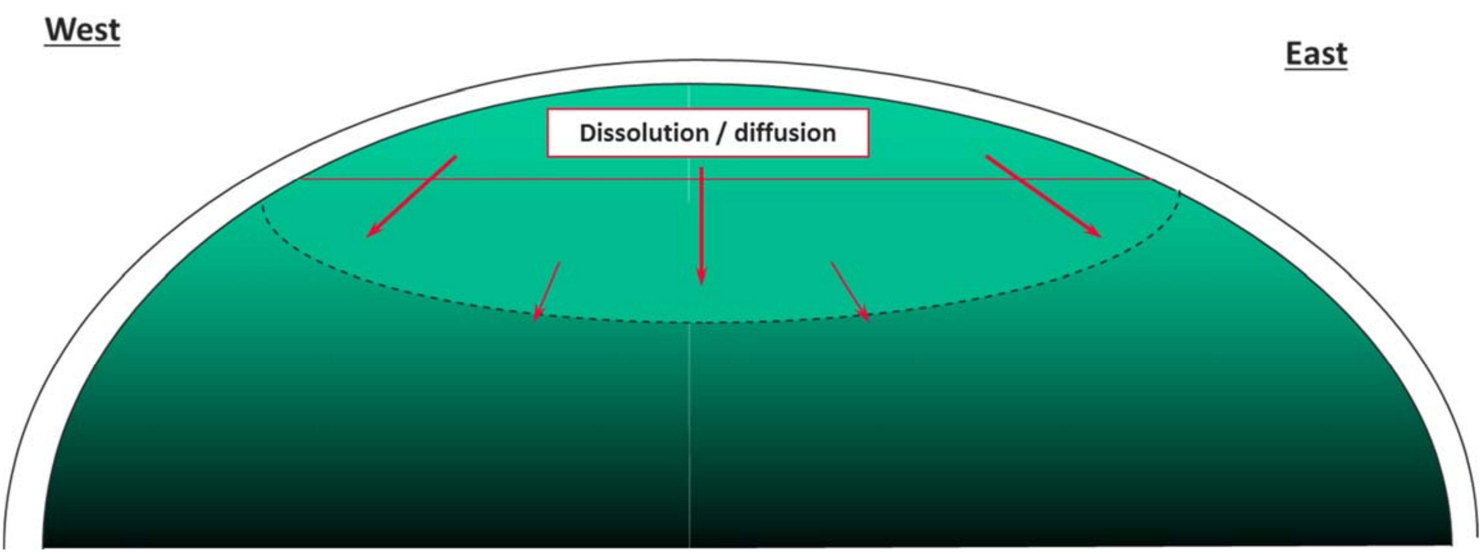
BHP # 460 b
BPP: top 330 b, top -70 m # 270 b

Field case / V



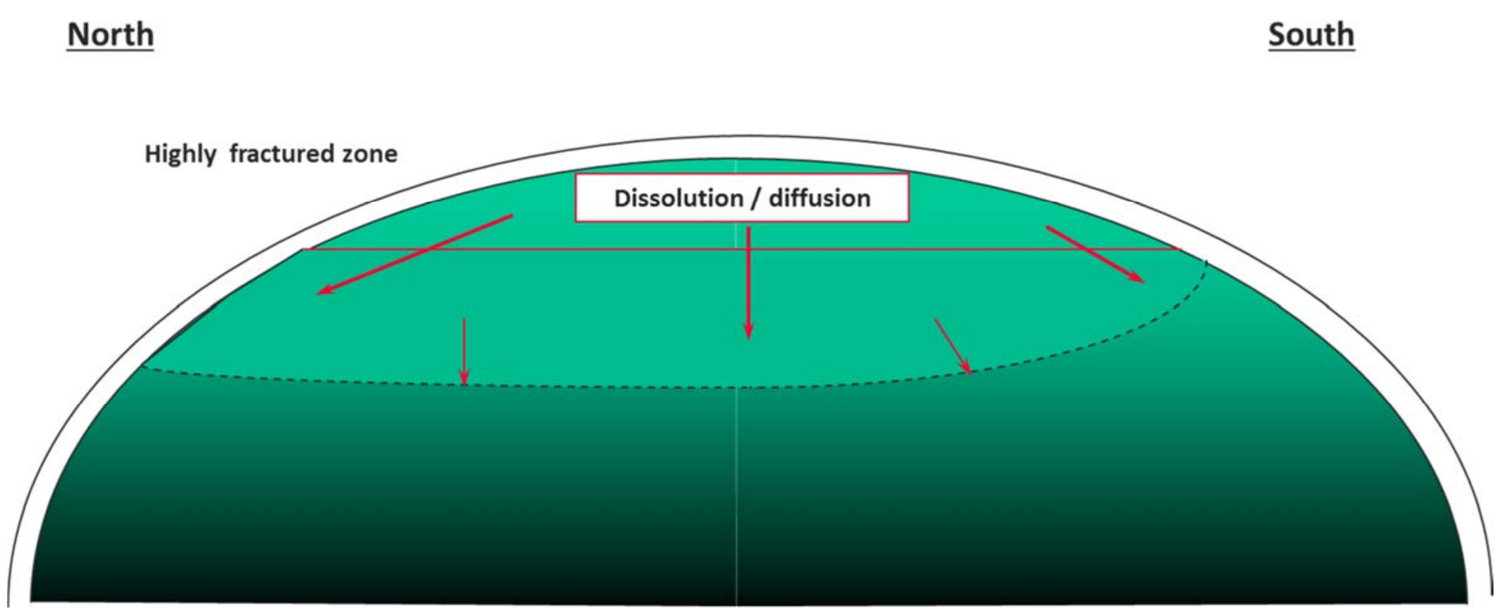
Paleo gas-cap dissolution

Field case / V



Paleo gas-cap dissolution

Field case / V



Paleo gas-cap dissolution

Field case / V

Today, the calculated diffusion mean distance is about 500 m

→ only a part of the reservoir has been highly affected by the dissolution / diffusion phenomenon

→ original fluid (not affected by the phenomenon) should be produced by the flank wells

Thermodynamic study

A differential liberation of a top fluid has been performed from bottom pressure to 250 b (accumulation pressure)

New calculation of the composition of the fluid obtained according to the depth in order to compare with the fluid flank

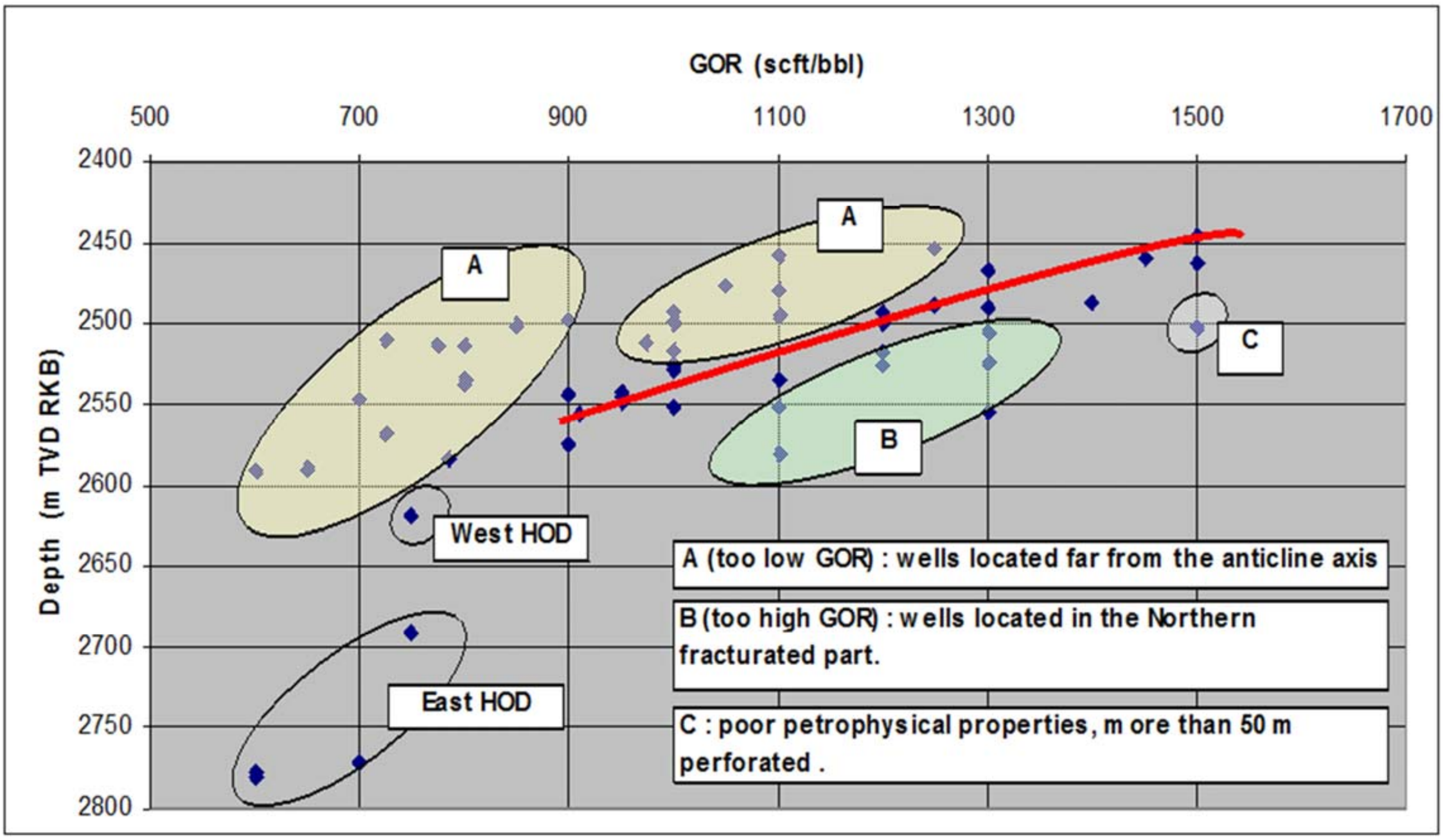
Gravitational model

Component	Composition top fluid	Diff. Lib. @ 90°C liquid phase (step 250 b)	Composition 37.5 m below @ 90°C	2/8 flank fluid	Composition 68 m below @ 91.1°C	2/11 flank fluid
N2	*0,66*	0,48	**0,48**	0,26	**0,47**	0,36
CO2	*0,35*	0,35	**0,35**	0,10	**0,35**	0,35
C1	*54,51*	46,40	**46,05**	44,86	**45,77**	45,68
C2	*7,88*	7,85	**7,82**	6,29	**7,80**	6,16
C3	*5,40*	5,76	**5,75**	5,92	**5,73**	6,17
IC4	*0,76*	0,84	**0,84**	0,88	**0,83**	0,83
NC4	*2,81*	3,16	**3,15**	3,54	**3,15**	3,50
IC5	*1,00*	1,15	**1,15**	1,34	**1,15**	1,54
NC5	*1,55*	1,80	**1,80**	1,89	**1,80**	2,17
C6	*1,91*	2,26	**2,26**	2,31	**2,26**	2,88
C7P	*23,17*	29,94	**30,35**	*32,61*	**30,68**	*30,36*

Conclusions

The classification of the GOR values can be explained according to:

the distance to the anticline axis,
the depth,
the fracturation level



Field case / G

Deep offshore field

PVT data

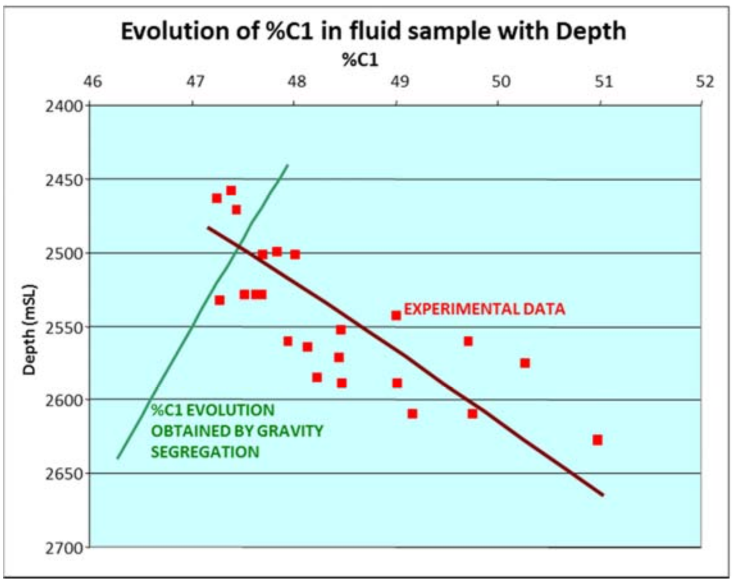
MDT pressures,

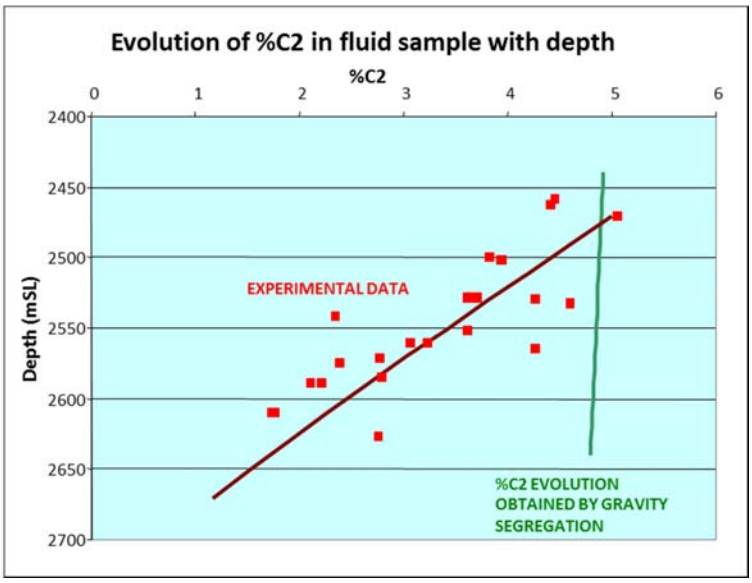
composition profile with depth

Continuous oil column

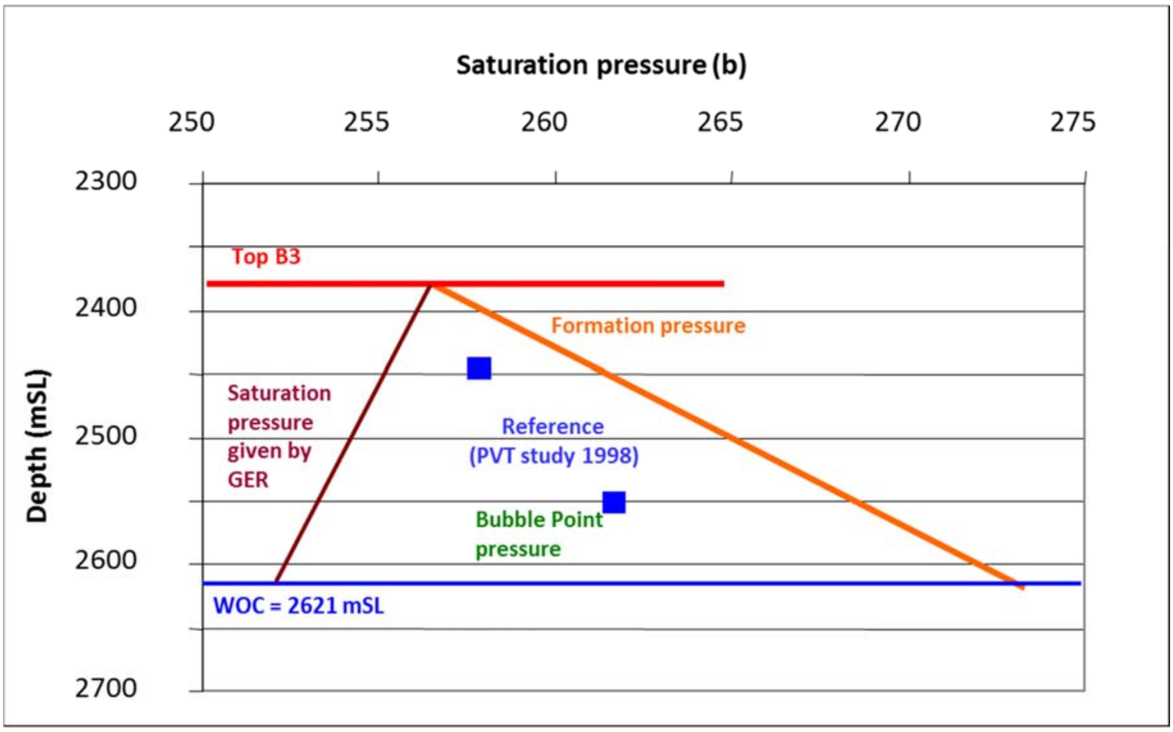
Field case / G

Non classical evolution with depth of some parameters





Non classical evolution with depth of some parameters



Data from geochemistry

very mature underlying source rock
producing gas

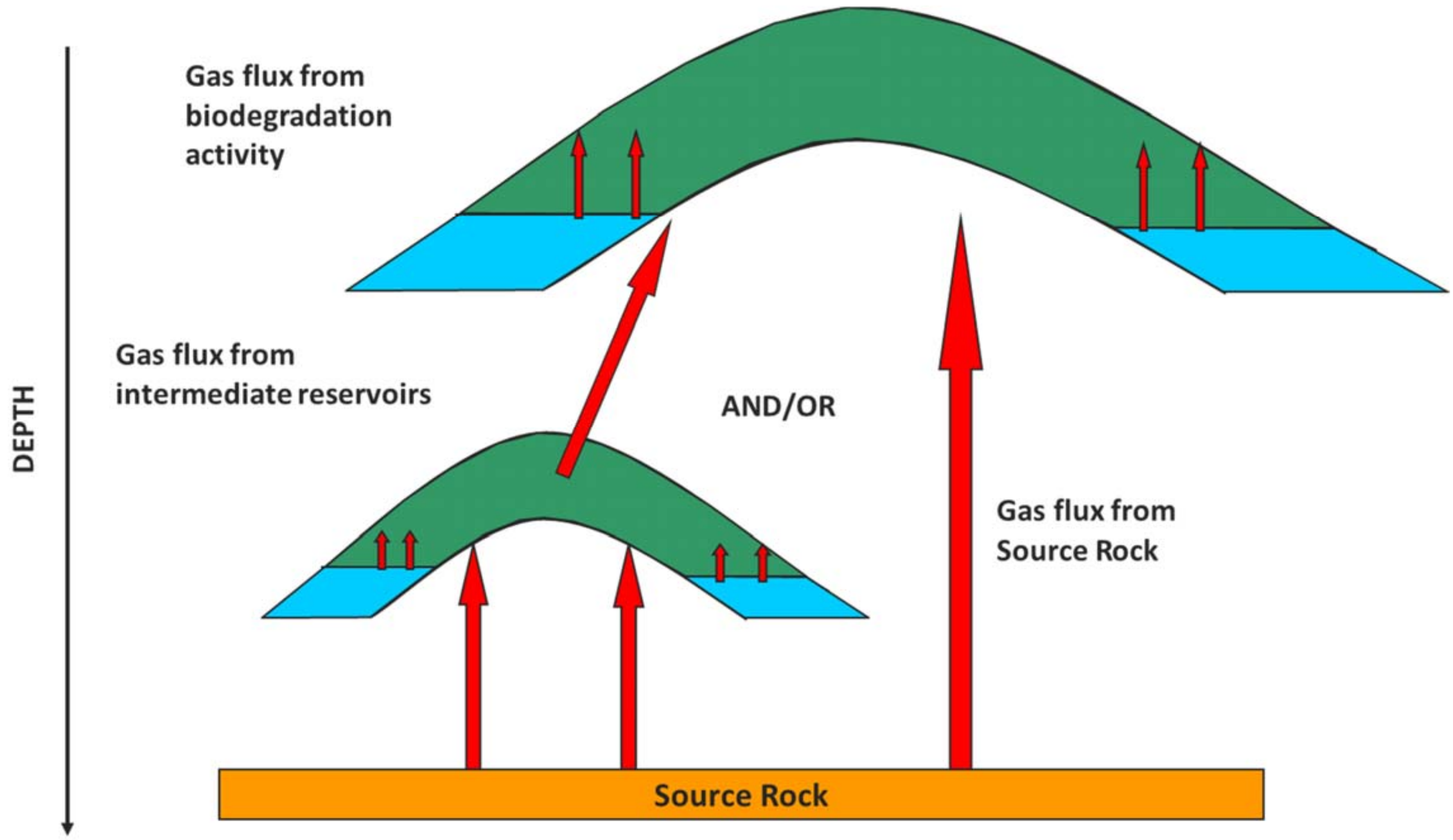
Data from GWD

non sealing cap-rock (C1 leakage)

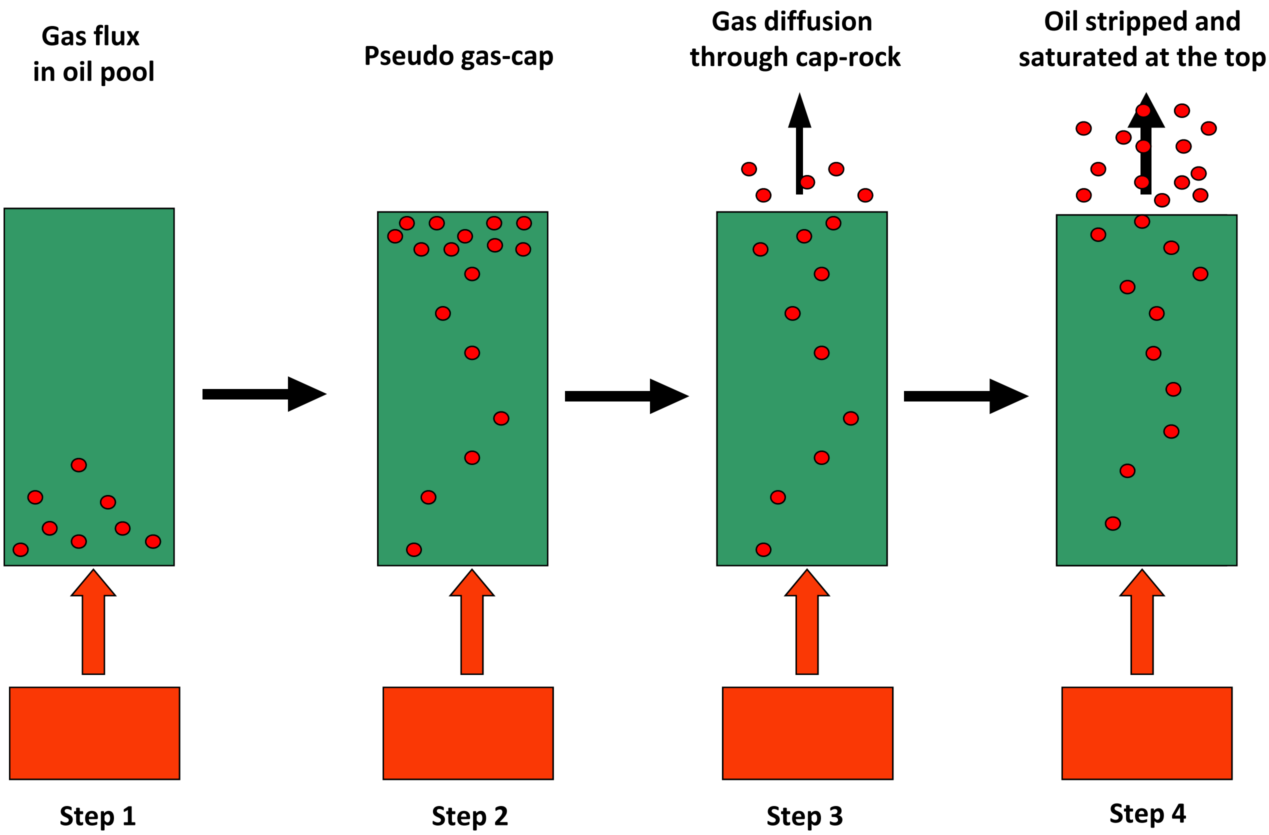
?

External gas flux

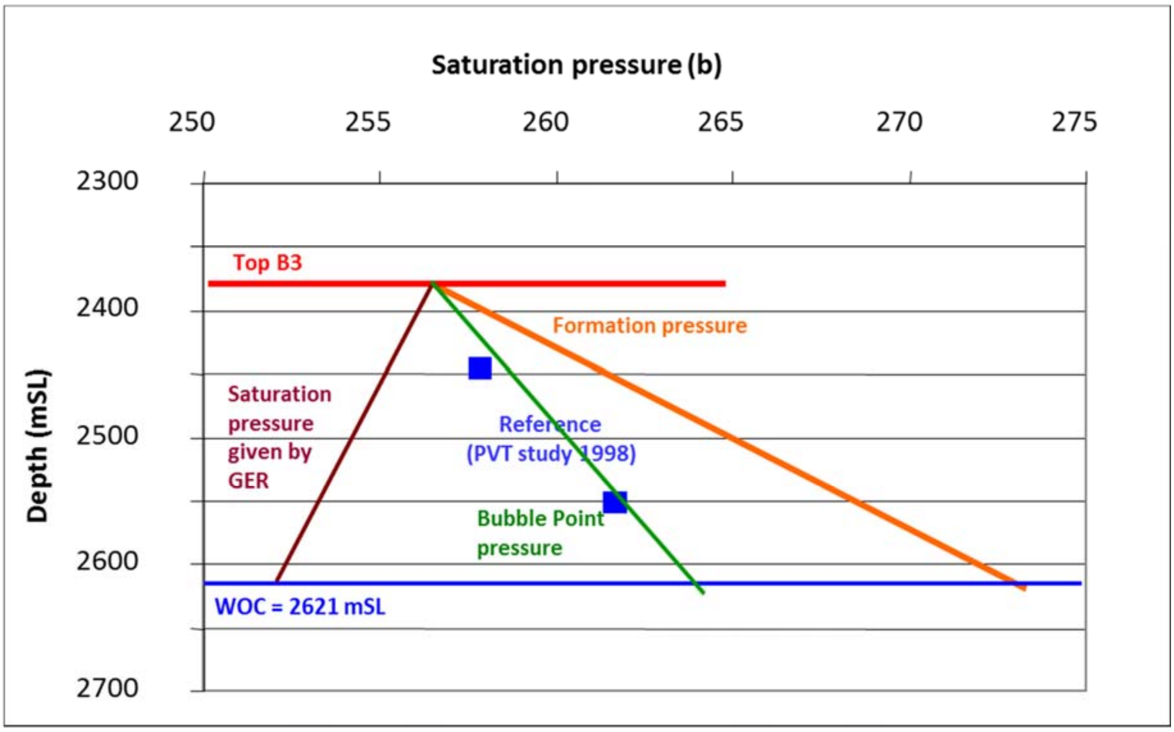
Field case / G



Field case / G



Field case / G



The non classical evolution has been explained and simulated by means of a partial gravitational model

Fluid studies PVT (Sampling – PVT)

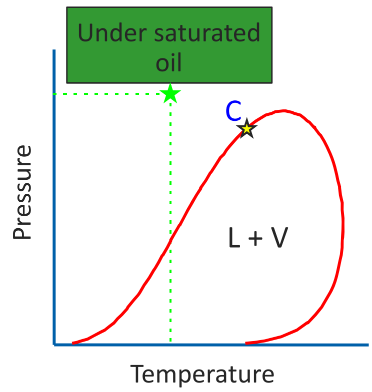
Quick sum up

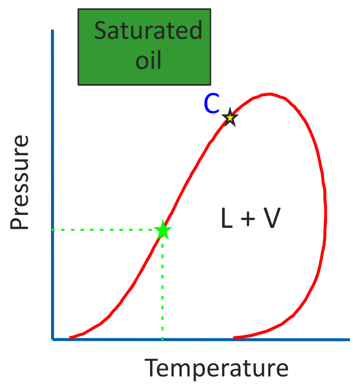
Reservoir fluid classification

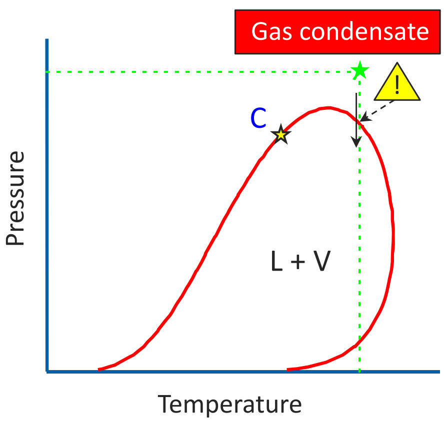
Oil system : T res < Tc

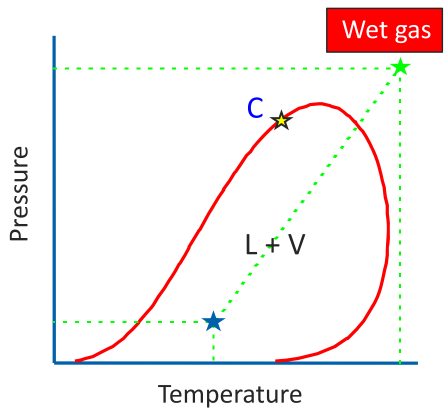
Gas system : T res > Tc

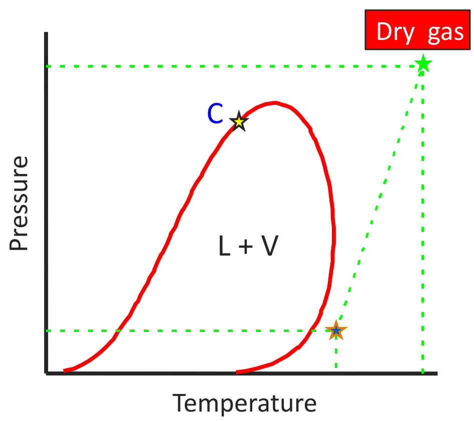
- ★ Initial reservoir Tres, Pres
- ★ Surface separator Ts, Ps
- ★ Critical point Tc, Pc





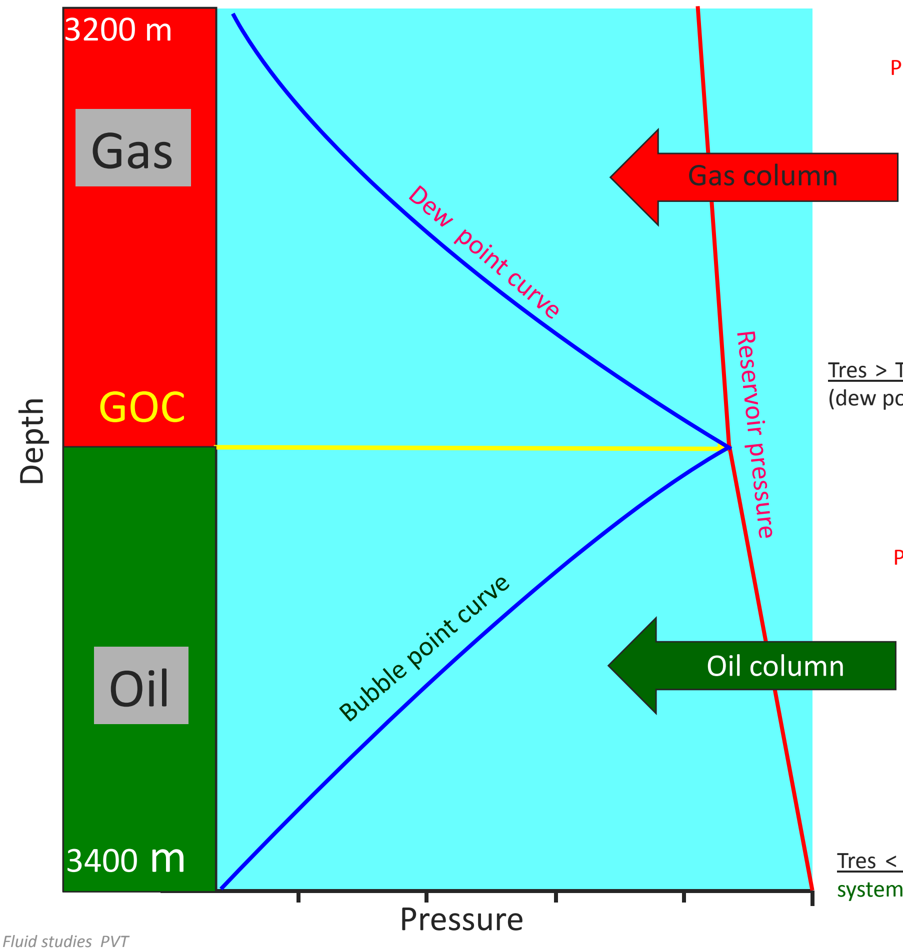


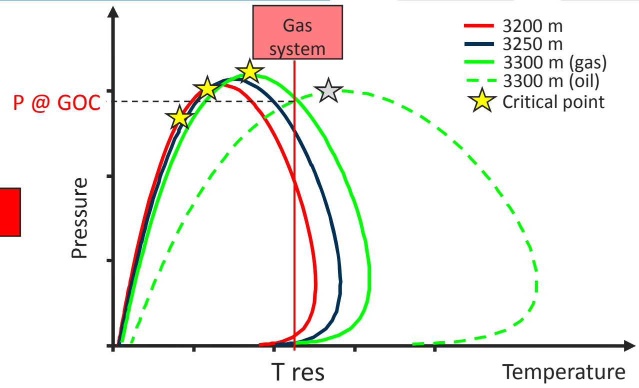




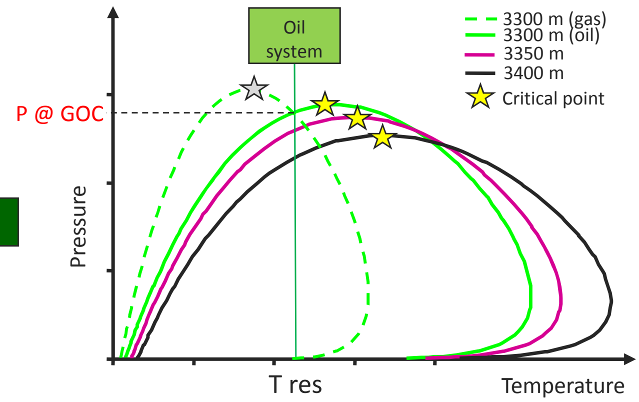
Water phase is not taken into account

Standard compositional grading with depth



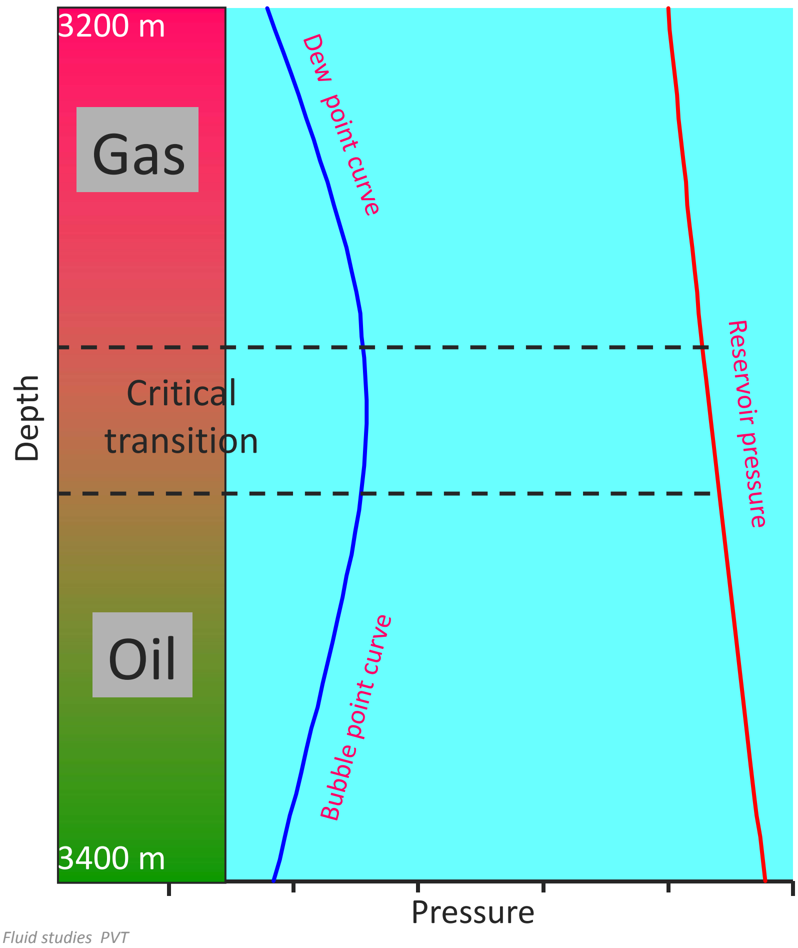


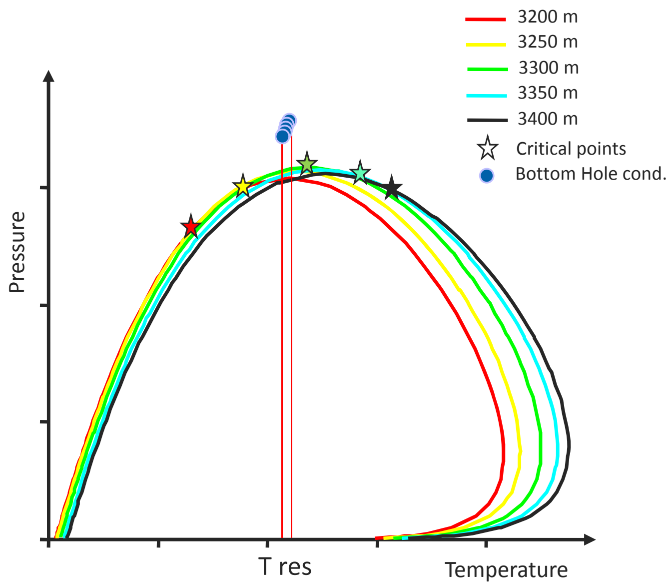
Tres > Tc of all the fluids in the hydrocarbon column ➔ gas system (dew point pressure increases with depth).



Tres < Tc of all the fluids in the hydrocarbon column ➔ oil system (bubble point pressure decreases with depth).

Critical transition without any GOC





Due to the displacement of the critical points, T res (~constant) which is higher than the corresponding Tc at the top, becomes lower at the bottom ➔ continuous change from a gas phase to an oil phase without any interface (no GOC).

None of the initial bottom hole conditions enters the phase envelop ➔ the reservoir fluid is always under monophasic state.

Sampling (1)

Cased Hole sampling

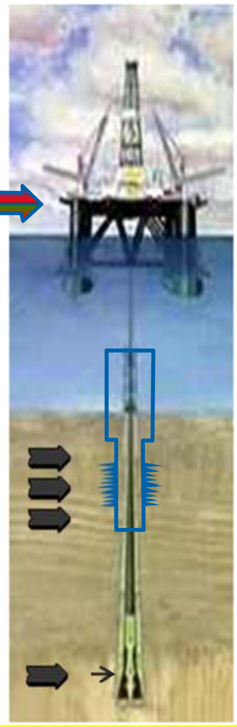
(Sampling after casing - during Testing (DST))

- Surface Sampling: → *Diphasic*
  - Well Head (monophasic)
  - Specific manifold
  - Separator
- Downhole Sampling:
  - Wireline
  - Chamber included in test assembly → *Monophasic*

Open Hole sampling

(Sampling before casing – while drilling – no flow at surface)

- Downhole Sampling: → *Monophasic*
  - MDT type (Schlumberger), RDT (Halliburton), RCI (Baker)



Downhole Sampling: the fluid is monophasic at sampling point, in open hole sampling the fluid may be polluted (after OBM drilling)

Sampling at surface: the fluid is generally diphasic

Sampling (2)

Reliable sampling

Whatever the technique: bottom hole flowing pressure > saturation pressure

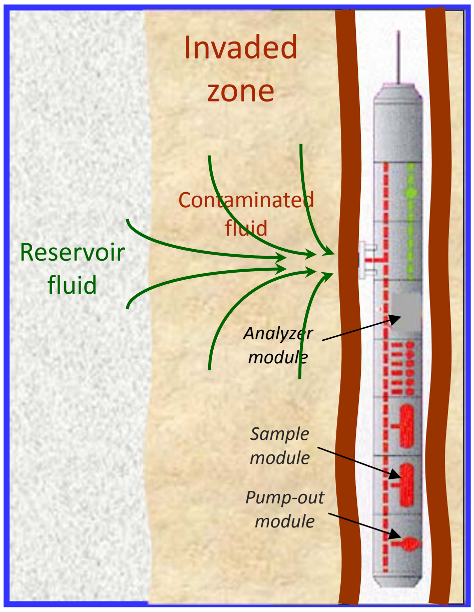
- **Bottom Hole Sampling (BHS):**
  - MDT type: fluid contamination (after an Oil Based Mud drilling) ➔ suitable corrections to get the properties of the actual reservoir fluid
  - DST: sampling tool location w.r.t perforations (segregation, liq-vap equilibrium)

- **Surface Sampling (separator):**
  - Constant GOR:
    - constant separator conditions (P, T)
    - lift up velocity for wet gases (v > 2-3 m/s to ensure the total liquid lift up)
  - Heater prior the separator input (to avoid wax deposit)
  - Separator efficiency (carry-over (wet gases), carry-under (heavy oils))

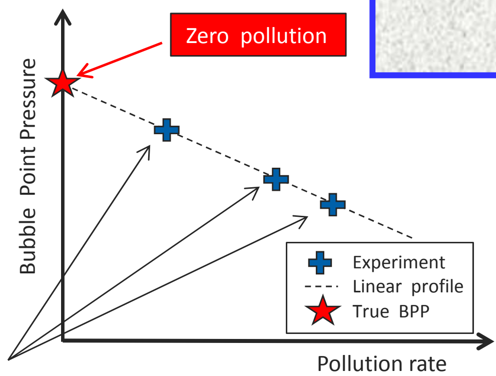
Sampling (3)

Open hole sampling after an OBM drilling

- **Fluid sample (MDT type) is contaminated by the hydrocarbons added to the mud,**
- **Whatever the pumping duration (for clean out), zero pollution is generally impossible,**
- **So, PVT experiments will be carried out on a contaminated fluid.**



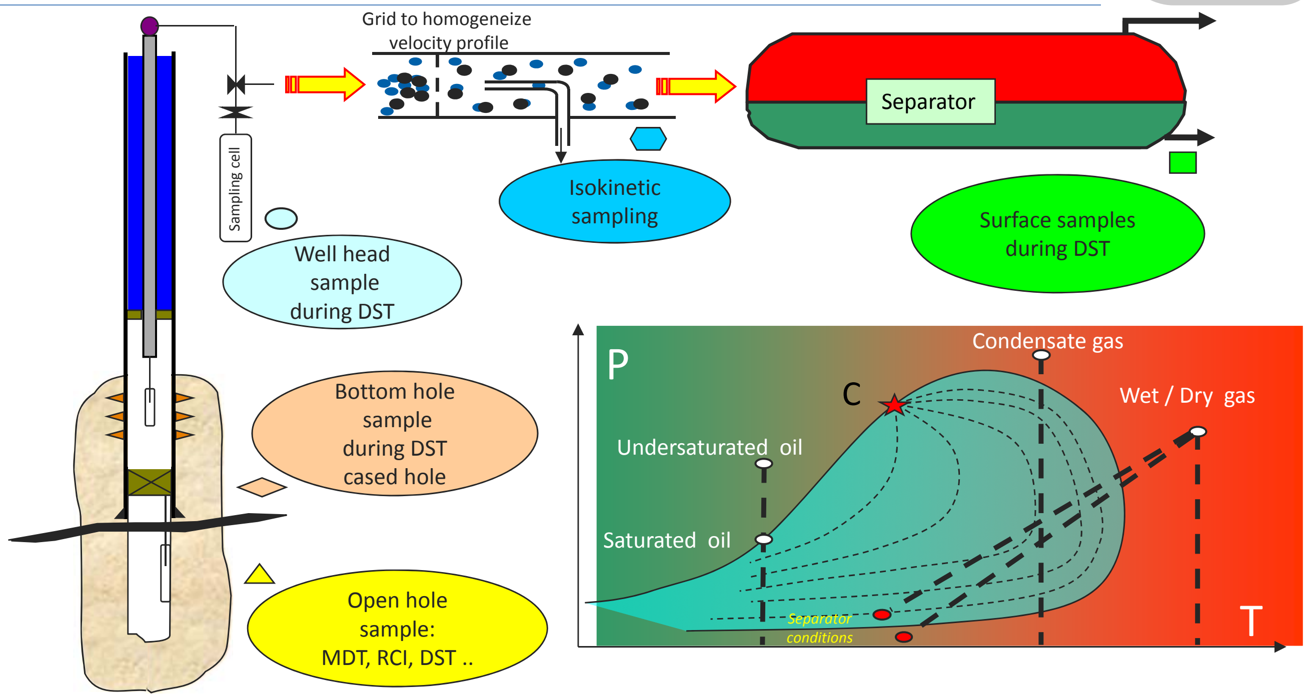
Do not use raw data from PVT study without any appropriate corrections

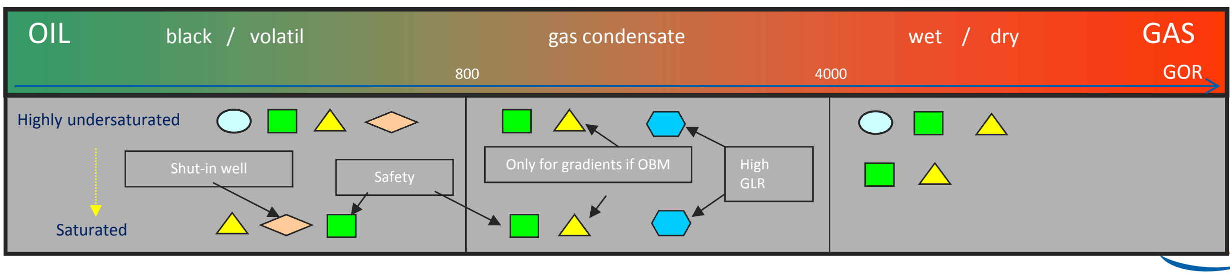


In order to determine the whole set of properties of the actual reservoir fluid

At a given depth, take 3 samples at different pollution rates.

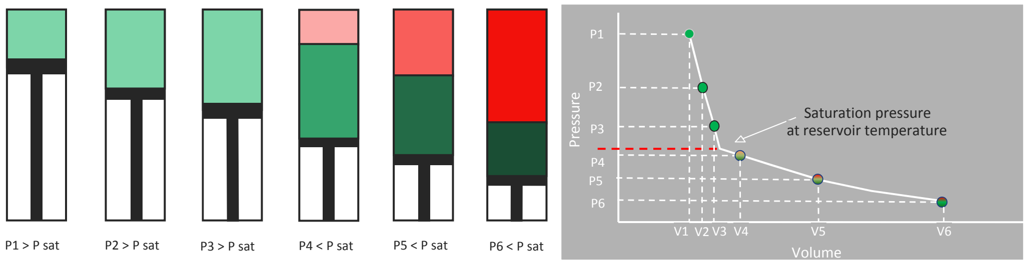
Sampling (4)



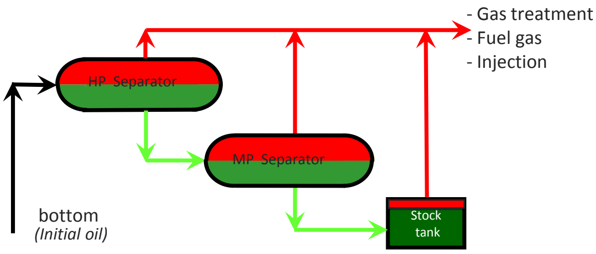


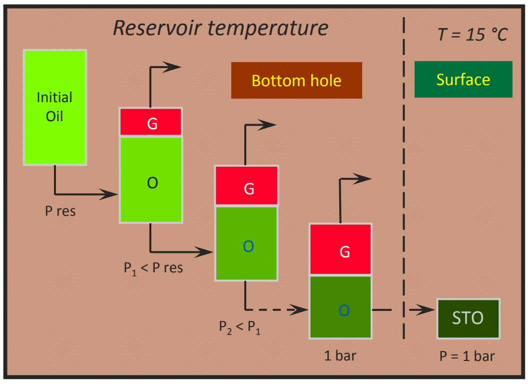
PVT experiments for oil

- **Constant mass expansion**
  - bubble point pressure



- **Multi-stage separation**
  - initial oil composition
  - initial oil density
  - initial oil process Rs
  - stock Tank Oil (STO) properties

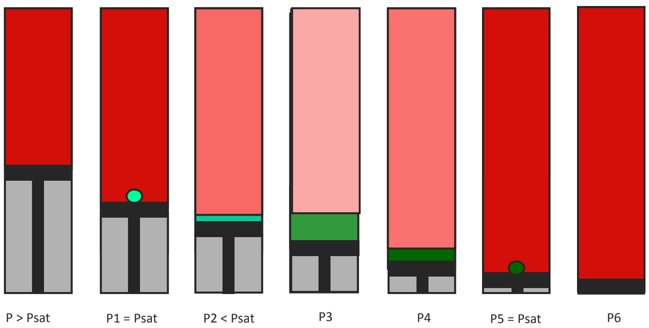


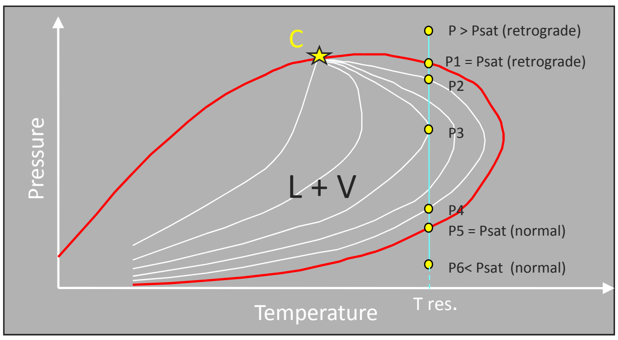


- **Differential vaporization** fluid properties vs Pressure
  - differential Bo function of P
  - differential Rs function of P
  - STO properties

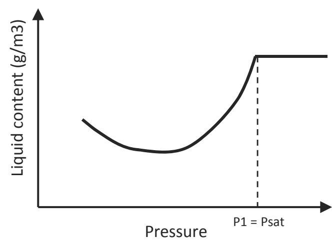
PVT experiments for gas condensate

- **Constant mass expansion (CME)**

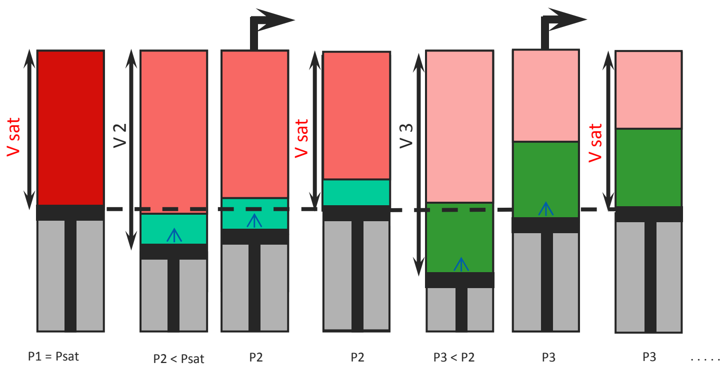


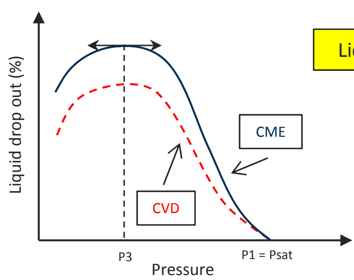


- **Constant volume depletion (CVD)**
  - very close to the actual behavior
  - produced gas composition function of P



Liquid content at surface (process)





Liquid deposit in the reservoir

Mechanisms

①

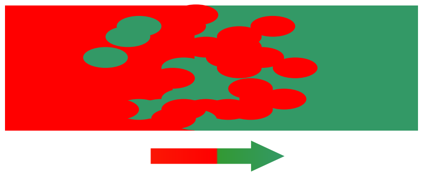
Change of So (➚) and μ (➘)

According to gas and oil composition also reservoir conditions:

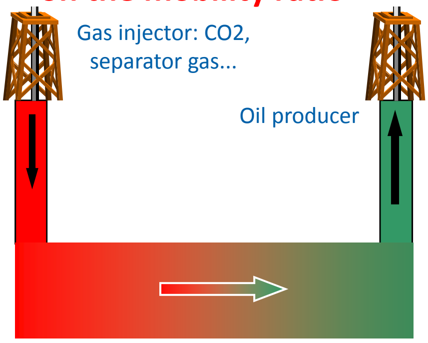
No miscibility: one phase → swelling effect depends on the undersaturated oil in the reservoir

② **According to gas and oil composition and also reservoir conditions:**

No miscibility: two phases →the sweeping efficiency depends on the mobility ratio



Front or fingerings

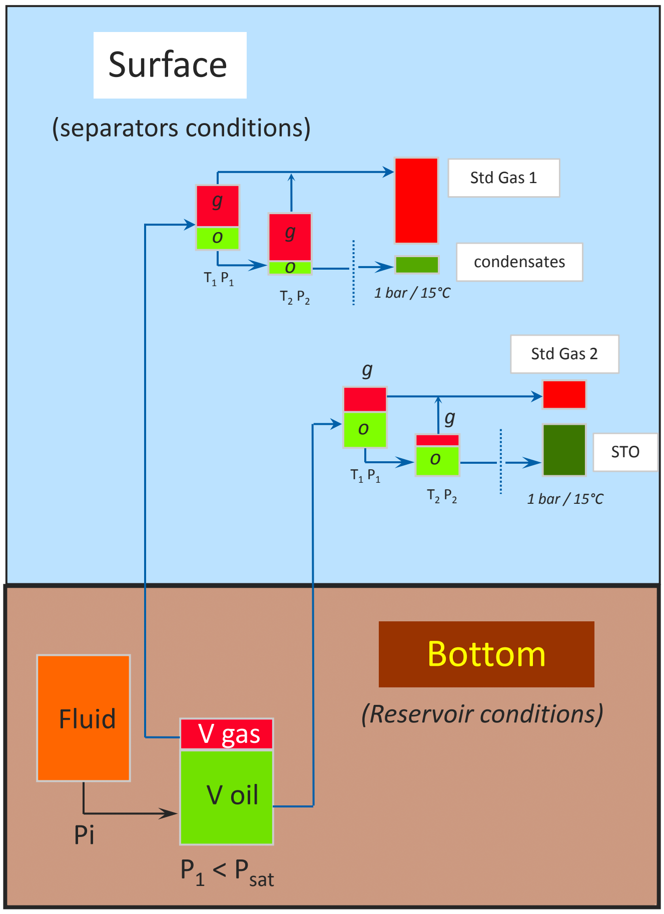


Progressive change from gas to oil

③

According to gas and oil composition and also reservoir conditions:

Miscibility is possible: obtaining of a progressive change → means Criticality



When the oil and gas reservoir phases run through surface facilities

For oil reservoir

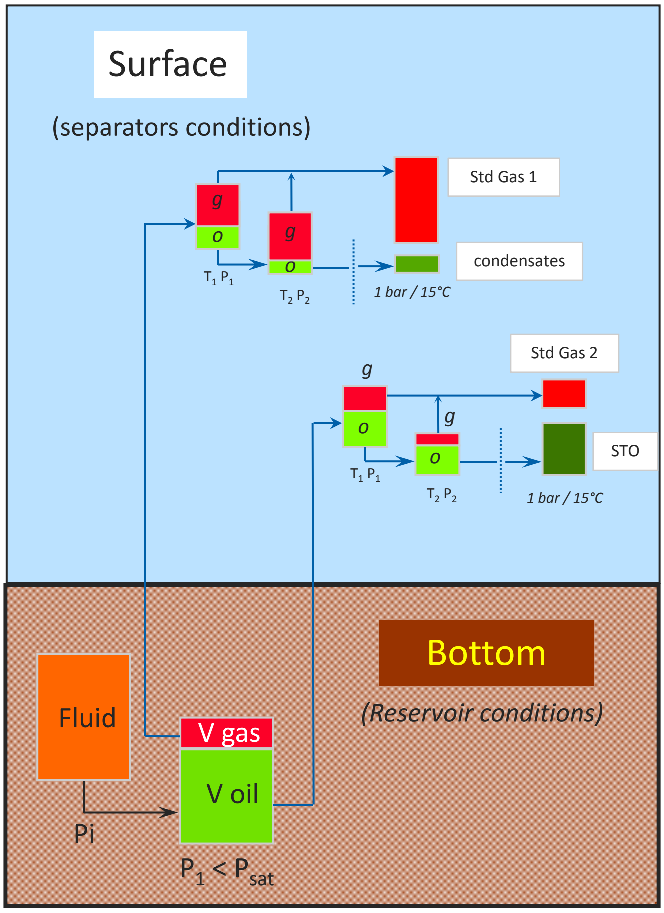
Bo = V oil / STO
Rs = Std Gas 2 / STO

For gas reservoir

Bg' = V gas / Std Gas 1
Rv = cgr = condensates / Std Gas 1
Bg = V gas / V gas in Std cond

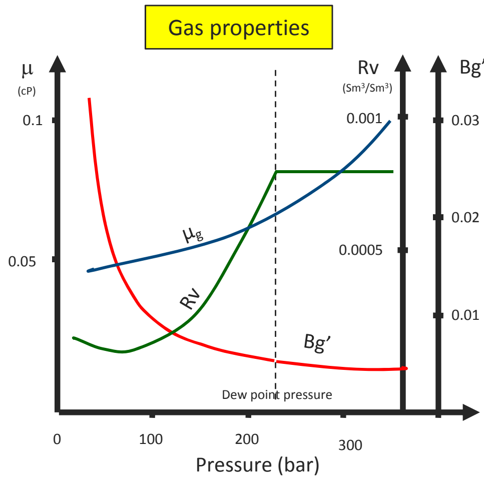
- Volumes at surface (1b/15°C) depend on the process scheme; so, Bo, Rs, Bg' and Rv depend on the process.
- Bg does not depend on the process.
- Except for dry gas, Bg is theoretical.
  - $Bg = (Z * T) / (288.15 * P)$ *T in K, P in bar*
  - $Bg \sim 1 / P$ *P in bar*
- As the reservoir pressure changes, oil and gas phases in the reservoir change too; so, Bo, Rs, Bg', Rv and Bg are functions of the reservoir pressure.

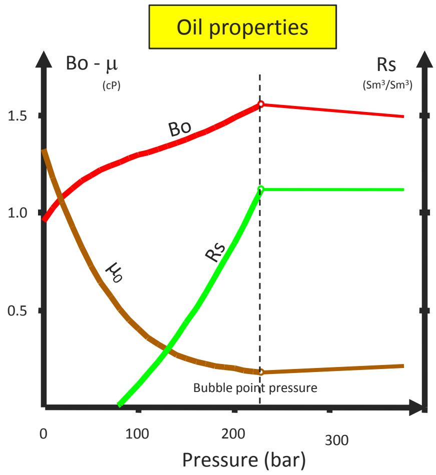
Definitions (2)



For gas reservoir

Bg' = V gas / Std Gas 1
Rv = condensates / Std Gas 1
Bg = V gas / V gas in Std cond





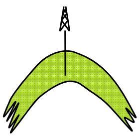
For oil reservoir

Bo = V oil / STO
Rs = Std Gas 2 / STO

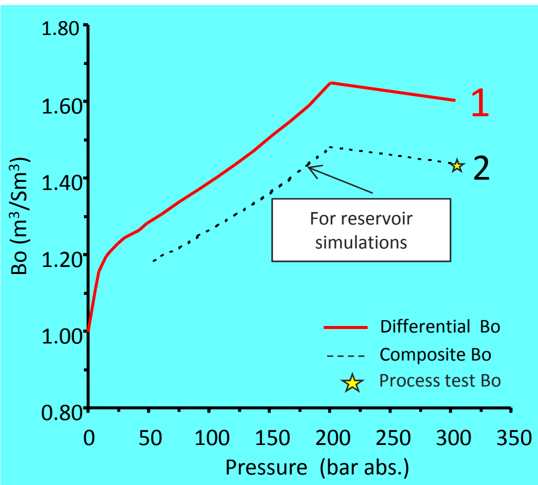
Calculation of STOIIP

How to calculate the Stock Tank Oil Initially In Place?

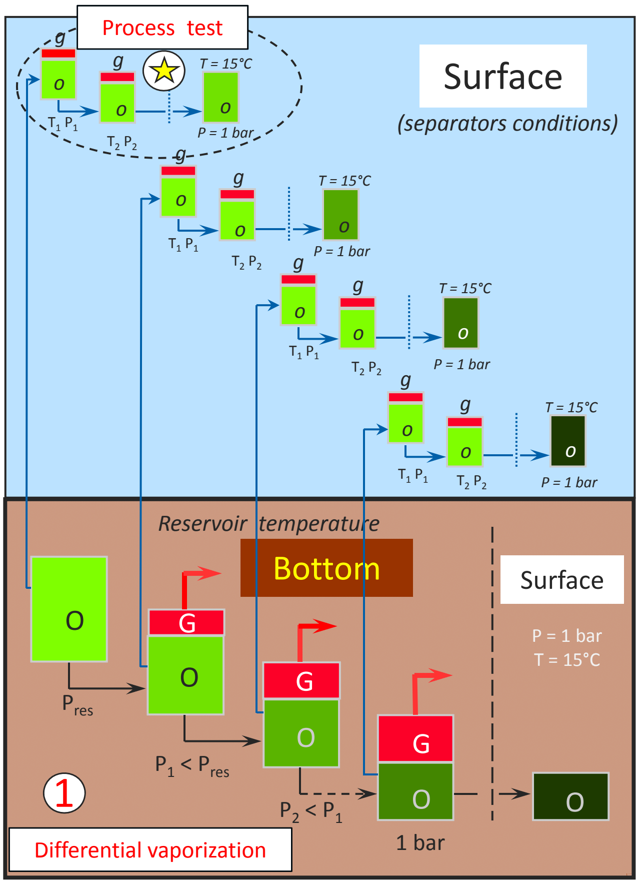
- **The geologist knows:**
  - the rock volume at reservoir condition (BHC)
  - the porosity (Φ) ➔ the fluid volume at BHC
  - the initial water saturation (Swi) and net to gross (Hu/Ht) ➔ the HC volume at BHC



STOIIP = HC volume @ BHC / initial process Bo



② = ① + ☆



Liquid — Vapor equilibrium

Thermodynamics constraints

- As per thermodynamics, at Liquid-Vapor equilibrium, some of the state functions display a minimum,
- In particular for G = H - T.S (T, P system) ➔ dG = - S.dT + V.dP = 0
- So that, for each component, Fugacity in liquid phase = Fugacity in vapor phase

Equation of state (EOS)

- Since Soave's improvement (1972) the fugacities can be accurately calculated by means of an EOS.
- The most widely used EOS is that of Peng & Robinson (1976):

$$\mathbf{P} = \frac{\mathbf{RT}}{\mathbf{V} - \mathbf{b}} - \frac{\mathbf{a}(\mathbf{T})}{\mathbf{V}(\mathbf{V} + \mathbf{b}) + \mathbf{b}(\mathbf{V} - \mathbf{b})}$$

Peng – Robinson's Equation

Pure component

$$\mathbf{P} = \frac{\mathbf{RT}}{\mathbf{V} - \mathbf{b}} - \frac{\mathbf{a}(\mathbf{T})}{\mathbf{V}(\mathbf{V} + \mathbf{b}) + \mathbf{b}(\mathbf{V} - \mathbf{b})}$$

$$\mathbf{a}(\mathbf{T}) = \mathbf{a}(\mathbf{T_c})\,\mathbf{f}(\mathbf{T})$$
$$\mathbf{a}(\mathbf{T_c}) = \Omega_a \frac{\mathbf{R^2 T_c^2}}{\mathbf{P_c}}$$
$$\Omega_a = \mathbf{0.4572}$$

$$\mathbf{b} = \mathbf{b}(\mathbf{T_c})$$
$$\mathbf{b}(\mathbf{T_c}) = \Omega_b \frac{\mathbf{R\,T_c}}{\mathbf{P_c}}$$
$$\Omega_b = \mathbf{0.0778}$$

$$\mathbf{f}(\mathbf{T}) = \left[\mathbf{1} + \mathbf{m}\left(\mathbf{1} - \sqrt{\mathbf{T_r}}\right)\right]^2$$

$\omega < 0.49$ (nC_{10})

$m = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$

$\omega > 0.49$

$m = 0.379642 + 1.48503\,\omega - 0.164423\,\omega^2 + 0.016666\,\omega^3$

Mixtures

$$P = \frac{RT}{V - b_m} - \frac{a_m(T)}{V(V + b_m) + b_m(V - b_m)}$$

$$b_m = \sum_{i=1}^{n} x_i \cdot b_i$$

$$a_m = \sum_{j=1}^{n}\sum_{i=1}^{n} x_i \cdot x_j \cdot (1 - k_{ij}) \cdot \sqrt{a_i \cdot a_j}$$

k_{ij} = Binary interaction coefficients

Fluid model

- **The fluid model is the whole characterization of all the components (Mw, Tc, Pc, w, volume shift, Vc, Parachor …) and the binary interaction coefficient matrix (Kij) obtained to perfectly fit the experimental data (PVT report).**
- **The fit is obtained by tuning the physical properties of the ''heavy'' cut(s), the Kij (between the lightest and the heaviest components) and the volume shift of the lightest and the heaviest component.**
  - Tc, Pc, ω, Kij to match the equilibrium (saturation pressure, composition),
  - Volume shift to match the volumes,
  - Vc to match the viscosity,
  - Parachor to match the interfacial tension.

BINARY INTERACTION COEFFICIENTS							
Kij	GN1	GN2	GN3	GN4	GN5	GN6	GN7
GN1		-0,00155	0,00032	0,00890	0,01851	0,05840	0,06738
GN2	-0,00155		0,00840	0,00137	0,00278	0,04802	0,04800
GN3	0,00032	0,00840		0,00146	0,00276	0,02998	0,02999
GN4	0,00890	0,00137	0,00146		0	0	0
GN5	0,01851	0,00278	0,00276	0		0	0
GN6	0,05840	0,04802	0,02998	0	0		0
GN7	0,06738	0,04800	0,02999	0	0	0	

COMPOSITION AND PHYSICAL PROPERTIES								
Name	ZF %	Mw	Tc (K)	Pc (bar)	Acent fact	Vol shift	Vc (cm^3)	Parachor
GN1	71,61	16,12	190,31	45,88	0,0116	-0,10	98,9	76,6995
GN2	11,19	31,28	301,25	49,65	0,0957	0	143,0	105,4330
GN3	7,11	48,95	387,44	40,49	0,1600	0	221,5	162,1903
GN4	3,87	84,05	506,62	32,49	0,2621	0	351,9	268,0716
GN5	2,27	122,66	618,15	26,34	0,3000	0	511,8	422,4642
GN6	3,11	204,81	702,45	18,50	0,6000	0	975,0	481,6625
GN7	0,84	340,00	787,25	17,50	0,9200	0,04	1320,0	799,5959